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(54) Title: ELECTROLUMINESCENT MATERIALS AND DEVICES

(57) Abstract: An improved electroluminescent device has a layer of a first electroluminescent metal complex or organo metallic complex and a layer of a second metal complex or organo metallic complex in which the band gap of the metal in the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the metal in the first electroluminescent metal complex or organo metallic complex.

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Electroluminescent Materials and Devices

The present invention relates to electroluminescent materials and to electroluminescent devices.

5

Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used; however these suffer from the disadvantages of high energy consumption, high cost
10 of manufacture, low quantum efficiency and the inability to make flat panel displays.

Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours; they are expensive to make and have a relatively low efficiency.

15

Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

20 Patent application WO98/58037 describes a range of transition metal and lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices
25 using rare earth chelates.

US Patent 5128587 discloses an electroluminescent device which consists of an organometallic complex of rare earth elements of the lanthanide series sandwiched between a transparent electrode of high work function and a second electrode of low

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work function with a hole conducting layer interposed between the electroluminescent layer and the transparent high work function electrode and an electron conducting layer interposed between the electroluminescent layer and the electron injecting low work function anode. The hole conducting layer and the
5 electron conducting layer are required to improve the working and the efficiency of the device. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

10

It is known that electroluminescent europium organometallic complexes emit light in the red part of the spectrum and application WO98/58037 discloses such complexes.

15

We have now devised an electroluminescent structure which gives improved red emission.

20

According to the invention there is provided an electroluminescent device which comprises (i) a first electrode, (ii) a layer of a first electroluminescent metal complex or organo metallic complex, (iii) a layer of a second metal complex or organo
metallic complex and (iv) a second electrode and in which the band gap of the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the first electroluminescent metal complex or organo metallic complex.

25

There can be more than one layer of each of the first and second electroluminescent metal complex or organo metallic complexes arranged alternatively.

30

In an electroluminescent organometallic complex when an electron drops from one level to a lower level, light is emitted and the larger the gap between the levels (the band gap) the higher the energy level difference and the shorter the wave length of the light emitted. Normally the metal in the second electroluminescent metal complex or organo metallic complex has a higher HOMO (highest occupied molecular orbital)

and a lower LOMO (lowest occupied molecular orbital) than the metal in the second electroluminescent metal complex or organo metallic complex.

5 The band gap of the second organometallic complex can be larger than the band gap of the first electroluminescent metal complex or organo metallic complex by virtue of the metals and/or organic ligands.

10 The metal in the first and second electroluminescent metal complex or organo metallic complex is preferably selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), U(III), U(VI)O₂, Tm(III), Th(IV), Ce (III), Ce(IV), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III).

15 Alternatively the thickness of the layer of the second electroluminescent metal complex or organo metallic complex is too thin to emit light, e.g. of less than 10 nanometres.

20 The metal in the first electroluminescent metal complex or organo metallic complex can be any metal which forms an electroluminescent metal complex or organo metallic complex, provided the band gap is less than the band gap of the organometallic complex in the second metal complex or organo metallic complex.

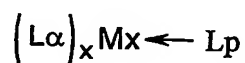
25 Preferred metals in the first electroluminescent metal complex or organo metallic complex are europium which emits light in the red region of the spectrum, terbium which emits light in the green region of the spectrum or dysprosium which emits light in the yellow region of the spectrum.

30 In the present invention the metal in the second electroluminescent metal complex or organo metallic complex is preferably gadolinium which emits light predominately in the ultra violet region of the spectrum. This has the advantage being that the ultra violet light emitted has no or a limited effect on the colour of the light emitted by the first electroluminescent metal complex or organo metallic complex; another preferred metal is cerium.

The first electroluminescent metal complex or organo metallic complex preferably has the formula $(L\alpha)_nM1$ where $L\alpha$ is an organic complex $M1$ is the metal and n is the valence state of $M1$.

- 5 The second electroluminescent metal complex or organo metallic complex preferably has the formula $(L\alpha)_nM2$ where $L\alpha$ is an organic complex $M2$ is the metal and n is the valence state of $M2$.

10 Preferred electroluminescent compounds which can be used in the present invention are of formula



(A)

15 where Mx is the metal, x is the valence state of Mx ; $L\alpha$ and Lp are organic ligands and Lp is a neutral ligand. The ligands $L\alpha$ can be the same or different and there can be a plurality of ligands Lp which can be the same or different.

20 For example $(L_1)(L_2)(L_3)Mx (Lp)$ where $(L_1)(L_2)(L_3)$ are the same or different organic complexes and (Lp) is a neutral ligand and the different groups $(L_1)(L_2)(L_3)$ may be the same or different.

Lp can be monodentate, bidentate or multidentate and there can be one or more ligands Lp .

25 The metal in the organometallic complex forming the first and second organometallic layers can be the same provided that the organic ligand is such that the band gap of the organometallic complex forming the second layer is larger than the band gap of the organometallic complex forming the first organometallic layer.

Further electroluminescent compounds which can be used in the present invention are of general formula $(L\alpha)_nMxM3$ where M3 is a non rare earth metal, $L\alpha$ is as herein and n is the combined valence state of Eu and M_2 . The complex can also comprise one or more neutral ligands L_p so the complex has the general formula
5 $(L\alpha)_nMxM3(L_p)$, where L_p is as herein. The metal M3 can be any metal which is not a rare earth, transition metal, lanthanide or an actinide. Examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony
10 (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states, e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

15 Preferred first electroluminescent metal complex or organo metallic complexes are $Eu(DBM)_3OPNP$ which has a band gap of 3.2eV and $Eu(TMHD)_3OPNP$ which has a band gap of 3.7 eV and a preferred gadolinium complex is $Gd(DBM)_3Phen$, where Phen is phenanthrene, which has a band gap of 3.8 eV.

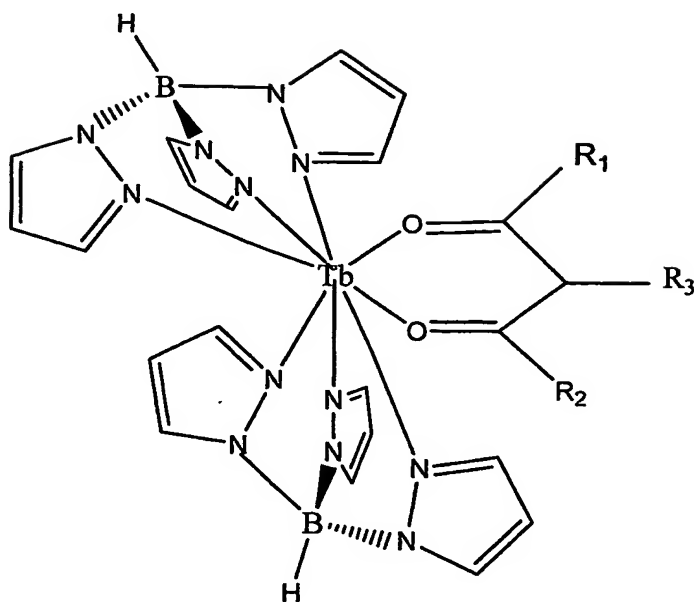
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For typical terbium complexes the band gap is of the order of 3.7eV.

In order to increase the conductivity of the second organometallic complex layer the layer can be doped with a conductivity improving additive such as a powdered metal,
25 conductive polymer.

Other complexes which can be used to form the second electroluminescent layer are organometallic complexes in which the organic ligand is a boron complex, e.g. of formula
30

- 6 -



- where R_1 and R_2 are the same or different and are hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R_1 , R_2 and R_3 are the same or different and are hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R_1 , R_2 and R_3 can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures, can be copolymerisable with a monomer, e.g. styrene or can be polymer, oligomer or dendrimer substituents.
- In place of the terbium other lanthanide, actinide or rare earth metals can be used.

The invention also provides further red emitters and according to this aspect of the invention there is provided an electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo

- 7 -

metallic complex mixed with an iridium metal complex or organo metallic complex and (iii) a second electrode.

5 There is preferably also a layer of an electroluminescent europium metal complex or organo metallic complex and the invention also provides electroluminescent devices of structures:-

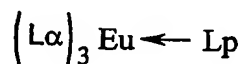
10 A. (i) a first electrode (ii) a layer of an electroluminescent europium metal complex or organo metallic complex (iii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex and (iv) a second electrode.

15 B. (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex, (iii) a layer of an electroluminescent europium metal complex or organo metallic complex and (iv) a second electrode.

20 C. (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo metallic complex, (iii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex, (iv) a layer of an electroluminescent europium metal complex or organo metallic complex and (v) a second electrode.

25 The electroluminescent europium metal complex or organo metallic complex preferably has the formula $(L\alpha)_3Eu$ where $L\alpha$ is an organic complex.

Preferred electroluminescent compounds which can be used in the present invention are of formula



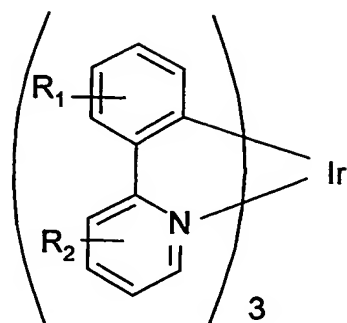
30

(AI)

where $L\alpha$ and Lp are organic ligands and Lp is a neutral ligand. The ligands $L\alpha$ can be the same or different and there can be a plurality of ligands Lp which can be the same or different.

- 5 For example $(L_1)(L_2)(L_3)Eu(Lp)$ where $(L_1)(L_2)(L_3)$ are the same or different organic complexes and (Lp) is a neutral ligand and the different groups $(L_1)(L_2)(L_3)$ may be the same or different, Lp can be monodentate, bidentate or multidentate and there can be one or more ligands Lp .
- 10 Further electroluminescent compounds which can be used in the present invention are of general formula $(L\alpha)_nEuM_2$ where M_2 is a non rare earth metal, $L\alpha$ is as herein and n is the combined valence state of Eu and M_2 . The complex can also comprise one or more neutral ligands Lp so the complex has the general formula $(L\alpha)_nEuM_2(Lp)$, where Lp is as herein. The metal M_2 can be any metal which is not a rare earth.
- 15 Lanthanide or an actinide examples of metals which can be used include lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, boron, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in
- 20 different valence states, e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, hafnium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.
- 25 A preferred europium complex is $Eu(DBM)_3OPNP$.

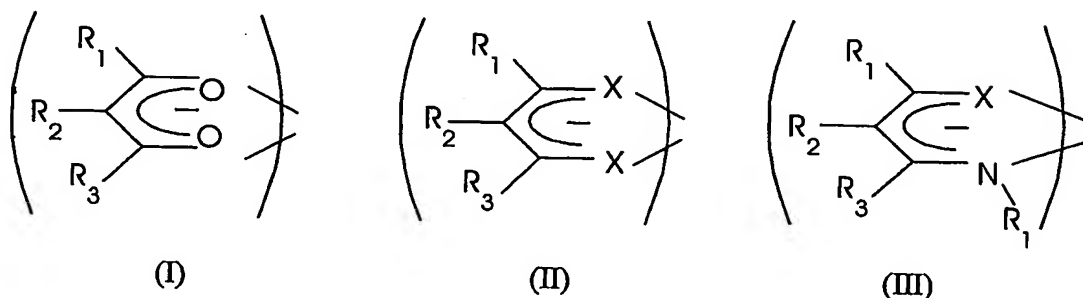
Preferred iridium complexes are iridium acetylacetonate, iridium di-acetylacetonate and $Ir(dpp)_3$



where R_1 and R_2 are as above.

Preferably $L\alpha$ is selected from β diketones such as those of formulae

5



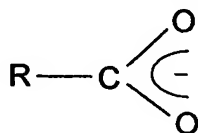
where R_1 , R_2 and R_3 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R_1 , R_2 and R_3 can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer, e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

- 10 -

Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

5

Some of the different groups L_α may also be the same or different charged groups such as carboxylate groups so that the group L_1 can be as defined above and the groups $L_2, L_3...$ can be charged groups such as



10

(IV)

where R is R_1 as defined above or the groups L_1, L_2 can be as defined above and $L_3...$ etc. are other charged groups.

R_1, R_2 and R_3 can also be



15

where X is O, S, Se or NH.

(V)

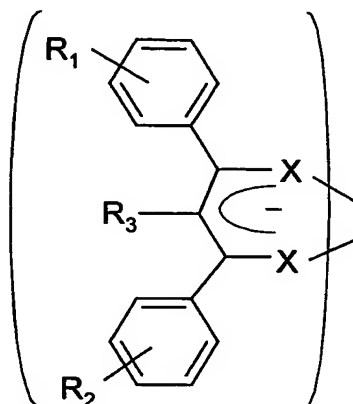
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A preferred moiety R_1 is trifluoromethyl CF_3 and examples of such diketones are, benzoyltrifluoroacetone, p-chlorobenzoyltrifluoroacetone, p-bromotrifluoroacetone, p-phenyltrifluoroacetone, 1-naphthoyltrifluoroacetone, 2-naphthoyltrifluoroacetone, 2-phenathoyltrifluoroacetone, 3-phenanthoyltrifluoroacetone, 9-anthroyltrifluoroacetone, cinnamoyltrifluoroacetone, and 2-thenoyltrifluoroacetone.

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- 11 -

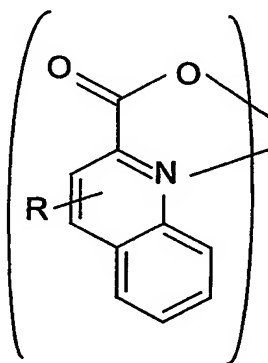
The different groups $L\alpha$ may be the same or different ligands of formulae



(VI)

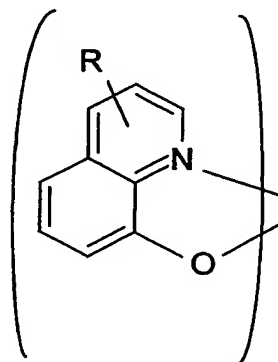
5 where X is O, S, or Se and R_1 , R_2 and R_3 are as above.

The different groups $L\alpha$ may be the same or different quinolate derivatives such as



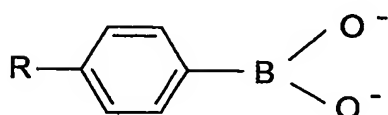
(VII)

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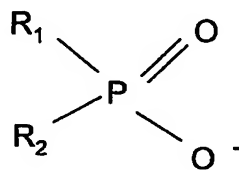
(VIII)

10 where R is hydrocarbyl, aliphatic, aromatic or heterocyclic carboxy, aryloxy, hydroxy or alkoxy, e.g. the 8 hydroxy quinolate derivatives or



(IX)

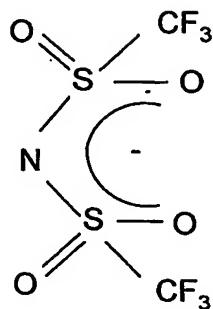
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(X)

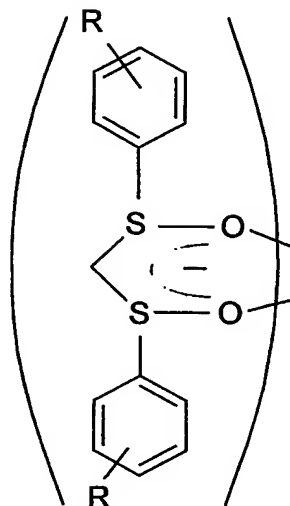
- 12 -

where R, R₁, and R₂ are as above or are H or F, e.g. R₁ and R₂ are alkyl or alkoxy groups



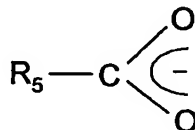
(XI)

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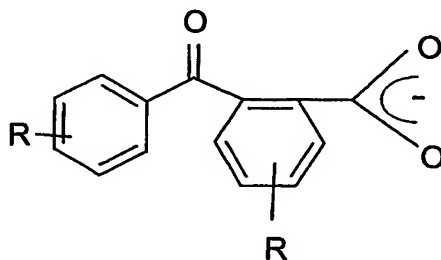
(XII)

- 5 As stated above the different groups L_α may also be the same or different carboxylate groups e.g.



(XIII)

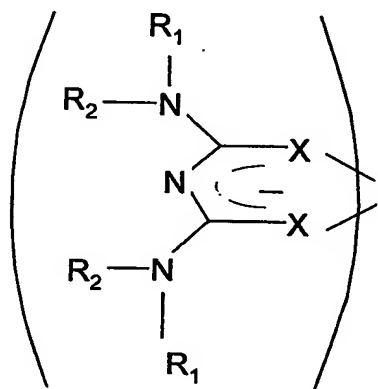
- where R₅ is a substituted or unsubstituted aromatic, polycyclic or heterocyclic ring a polypyridyl group, R₅ can also be a 2-ethyl hexyl group so L_n is 2-ethylhexanoate or R₅ can be a chair structure so that L_n is 2-acetyl cyclohexanoate or L_α can be
- 10



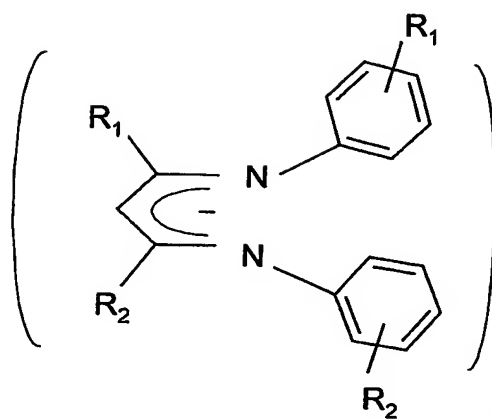
(XIV)

where R is as above, e.g. alkyl, allenyl, amino or a fused ring such as a cyclic or polycyclic ring.

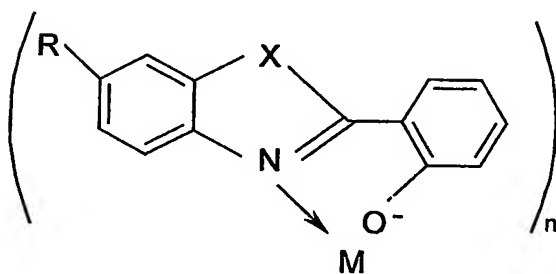
5 The different groups $L\alpha$ may also be



or

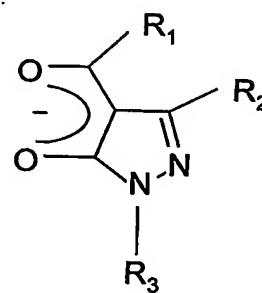


or



where X is O, S or Se

(XVII)

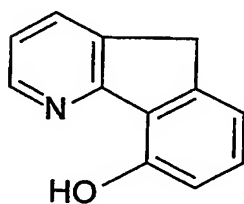


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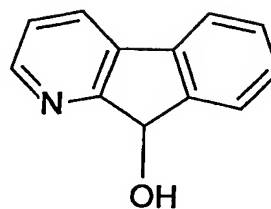
(XVIIa)

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where R, R_1 and R_2 are as above or

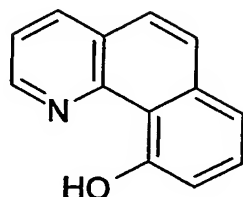


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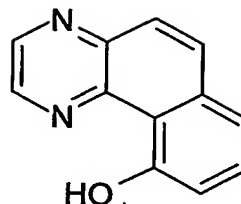
(XVIIc)

- 14 -



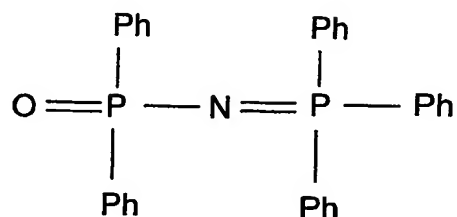
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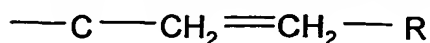
(XVIIe)

- 5 The groups L_P in the formula (A) above can be selected from



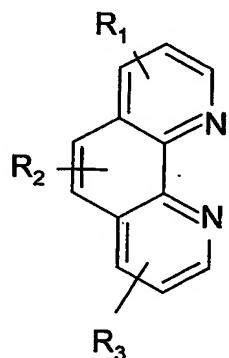
(XVIII)

- 10 where each Ph which can be the same or different and can be a phenyl (OPNP) or a substituted phenyl group, other substituted or unsubstituted aromatic group, a substituted or unsubstituted heterocyclic or polycyclic group, a substituted or unsubstituted fused aromatic group such as a naphthyl, anthracene, phenanthrene or pyrene group. The substituents can be, for example, an alkyl, aralkyl, alkoxy, aromatic, heterocyclic, polycyclic group, halogen such as fluorine, cyano, amino, substituted amino etc. Examples are given in figs. 1 and 2 of the drawings where R,
- 15 R_1 , R_2 , R_3 and R_4 can be the same or different and are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R , R_1 , R_2 , R_3 and R_4 can also form substituted
- 20 and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer, e.g. styrene. R , R_1 , R_2 , R_3 and R_4 can also be unsaturated alkylene groups such as vinyl groups or groups

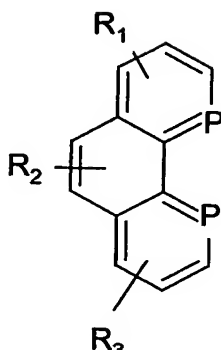


where R is as above.

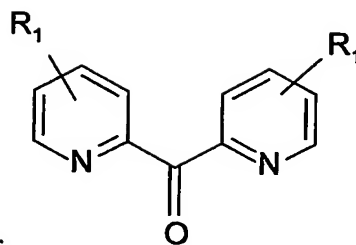
L_p can also be compounds of formulae



(XVIV)



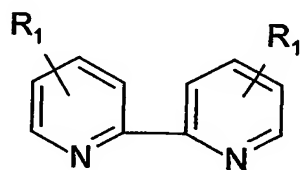
(XX)



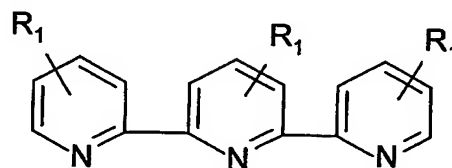
(XXI)

5

where R_1 , R_2 and R_3 are as referred to above, for example bathophen shown in fig. 3 of the drawings in which R is as above or



(XXII)



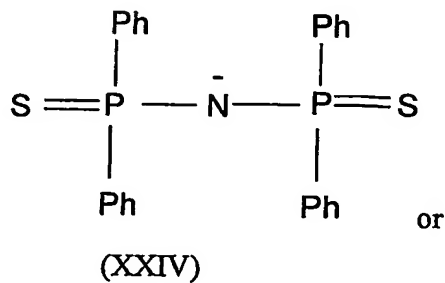
(XXIII)

10

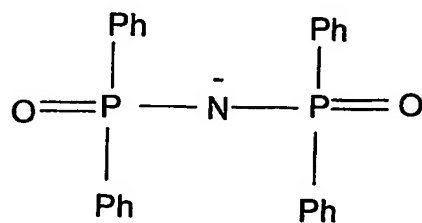
where R_1 , R_2 and R_3 are as referred to above.

L_p can also be

15



(XXIV)



(XXV)

- 16 -

where Ph is as above.

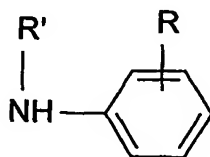
Other examples of L_p chelates are as shown in figs. 4 and fluorene and fluorene derivatives, e.g. as shown in fig. 5 and compounds of formulae as shown in figs. 6 to 8.

Specific examples of L_α and L_p are tripyridyl and TMHD, and TMHD complexes, $\alpha, \alpha', \alpha''$ tripyridyl, crown ethers, cyclans, cryptans phthalocyanans, porphoryins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA, where TMHD is 2,2,6,6-tetramethyl-3,5-heptanedionato and OPNP is diphenylphosphonimide triphenyl phosphorane. The formulae of the polyamines are shown in fig. 11.

The first electrode can function as the cathode and the second electrode can function as the anode and preferably there is a layer of a hole transporting material between the anode and the layer of the electroluminescent compound.

The hole transporting material can be any of the hole transporting materials used in electroluminescent devices.

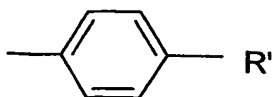
The hole transporting material can be an amine complex such as poly (vinylcarbazole), N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), an unsubstituted or substituted polymer of an amino substituted aromatic compound, a polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes etc. Examples of polyanilines are polymers of



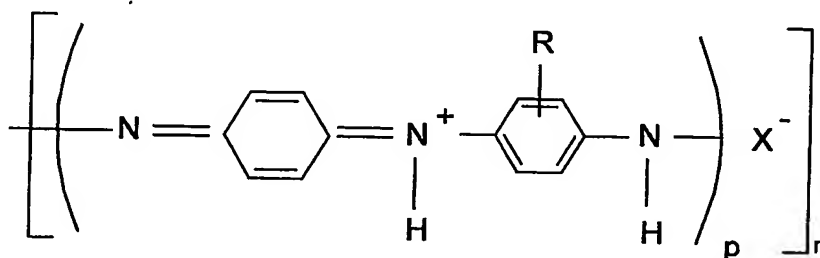
(XXVI)

- 17 -

where R is in the ortho - or meta-position and is hydrogen, C1-18 alkyl, C1-6 alkoxy, amino, chloro, bromo, hydroxy or the group



5 where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula I above, or the hole transporting material can be a polyaniline; polyanilines which can be used in the present invention have the general formula



(XXVII)

10 where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO₄, BF₄, PF₆, H₂PO₃, H₂PO₄, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulose sulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

15 Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinone-sulphonate and anthracenesulphonate. An example of an arenedicarboxylate is phthalate and an example of arenecarboxylate is benzoate.

20 We have found that protonated polymers of the unsubstituted or substituted polymer of an amino substituted aromatic compound such as a polyaniline are difficult to evaporate or cannot be evaporated, however we have surprisingly found that if the unsubstituted or substituted polymer of an amino substituted aromatic compound is deprotonated then it can be easily evaporated, i.e. the polymer is evaporable.

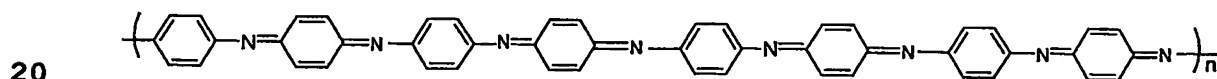
Preferably evaporable deprotonated polymers of unsubstituted or substituted polymer of an amino substituted aromatic compound are used. The de-protonated unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali such as ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319 1989.

The conductivity of the polyaniline is dependant on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60%, e.g. about 50%.

Preferably the polymer is substantially fully deprotonated.

A polyaniline can be formed of octamer units i.e. p is four e.g.



The polyanilines can have conductivities of the order of 1×10^{-1} Siemen cm^{-1} or higher.

The aromatic rings can be unsubstituted or substituted, e.g. by a C1 to 20 alkyl group such as ethyl.

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The polyaniline can be a copolymer of aniline and preferred copolymers are the copolymers of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with amino anthracenes.

5

Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonaphthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic compound. Polyaminoanthracenes and methods of making them are disclosed in US
10 Patent 6,153,726. The aromatic rings can be unsubstituted or substituted, e.g. by a group R as defined above.

15

Other hole transporting materials are conjugated polymer and the conjugated polymers which can be used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

20

The preferred conjugated polymers are poly (p-phenylenevinylene)-PPV and copolymers including PPV. Other preferred polymers are poly(2,5 dialkoxyphenylene vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene),
poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

25

In PPV the phenylene ring may optionally carry one or more substituents, e.g. each independently selected from alkyl, preferably methyl, alkoxy, preferably methoxy or ethoxy.

Any poly(arylenevinylene) including substituted derivatives thereof can be used and the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring system such as anthracene or naphthylene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased, e.g. up to 7 or higher.

5

The conjugated polymers can be made by the methods disclosed in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The thickness of the hole transporting layer is preferably 20nm to 200nm.

10

The polymers of an amino substituted aromatic compound such as polyanilines referred to above can also be used as buffer layers with or in conjunction with other hole transporting materials.

15 The structural formulae of some other hole transporting materials are shown in Figures 12 to 16 of the drawings, where R_1 , R_2 and R_3 can be the same or different and are selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R_1 , R_2 and R_3 can
20 also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer, e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures,
25 fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl,

biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

- Optionally there is a layer of an electron injecting material between the cathode and the electroluminescent material layer. The electron injecting material is a material which will transport electrons when an electric current is passed through electron injecting materials include a metal complex such as a metal quinolate, e.g. an aluminium quinolate, lithium quinolate, $Mx(DBM)_n$ where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx, e.g Mx is aluminium or chromium.
- 5 The electron injecting material can also be a cyano anthracene such as 9,10 dicyano anthracene, cyano substituted aromatic compounds, tetracyanoquinidodimethane a polystyrene sulphonate or a compound with the structural formulae shown in figures 9 or 10 of the drawings in which the phenyl rings can be substituted with substituents R as defined above. Instead of being a separate layer the electron injecting material
- 10 can be mixed with the electroluminescent material and co-deposited with it.
- 15

Optionally the hole transporting material can be mixed with the electroluminescent material and co-deposited with it.

- 20 The hole transporting materials, the electroluminescent material and the electron injecting materials can be mixed together to form one layer, which simplifies the construction.

- The anode is preferably a transparent substrate such as a conductive glass or plastic material which acts as the anode; preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer such as a metal or conductive polymer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate.
- 25

The cathode is preferably a low work function metal e.g. aluminium, calcium, lithium, magnesium and alloys thereof such as silver/magnesium alloys, rare earth metal alloys etc; aluminium is a preferred metal. A metal fluoride such as an alkali
5 metal, rare earth metal or their alloys can be used as the second electrode, for example by having a metal fluoride layer formed on a metal.

The invention is illustrated in the examples.

Example 1

10 An example of an electroluminescent device according to the invention is shown in figs. 17a, 17b. of the drawings. A pre-etched ITO coated glass piece ($10 \times 10\text{cm}^2$) was used. The device was fabricated by sequentially forming layers on the ITO, by vacuum evaporation using a Solciet Machine, ULVAC Ltd. Chigacki, Japan; the active area of each pixel was 3mm by 3mm.

15

In fig. 17a on the ITO coated glass anode (1) there are layers in which (2) is a hole transporting layer of TPD, (3) is a layer of $\text{Eu}(\text{DBM})_3\text{OPNP}$ (R1), (4) is a layer of $\text{Gd}(\text{tmhd})_3\text{Phen}$, (5) is an electron transmitting layer of aluminium quinolate, (6) is a lithium fluoride layer and (7) is an aluminium cathode.

20

When an electric current is passed through the device red light is emitted via (1).

Various structures were formed and the colour coordinates x:y and their peak efficiencies measured and the results shown in Table 1. The colour coordinates are as
25 on the CIE 1931 Chart.

- 23 -

Table 1

Reference	Cd/m ²	Cd/A	x	y
1	2.4	1.13	0.66	0.33
2	15.4	2.01	0.66	0.33
3	0.9	3.13	0.66	0.33

where 1 is –

5 ITO/TPD(35.5nm)/R1(23.6nm)/Gd(tmhd)₃Phen(20.3nm)/R1(24.2nm)/Alq3(15.5nm)/Al

2 is –

ITO/TPD(33nm)/R1(23nm)/Gd(tmhd)₃Phen(10nm)/R1(10nm)/
Gd(tmhd)₃Phen(10nm)/R1(23nm) Alq3(9nm)/Al

10 3 is –

ITO/DFDAA(13nm)/ TPD(33nm)/ R1(23nm)/Gd(tmhd)₃Phen(10nm)/ R1(10nm)/
Gd(tmhd)₃Phen(10nm)/R1(23nm) Alq3(9nm)/Al

where R1 is Eu(DBM)₃OPNP and DFDAA is a buffer layer.

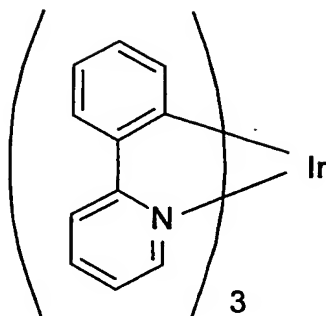
15 Example 2

An electroluminescent device shown in fig. 17a was formed. As in example 1 there are layers 1 to 7 where (1) is ITO, (2) is CuPc (3) is α -NPB (4) is the electroluminescent mixture (5) is Eu(DBM)₃OPNP (6) is Alq₃ (7) is Al to form :-

ITO/CuPc(8nm)/ α -NPB(40nm)/R1(10nm)/ CBP +Ir(dpp)₃(6%)+ R1(40%)(20nm)
20 /R1(20nm)/BCP(6nm)/Alq3(20nm)/Al

where R1 is Eu(DBM)₃OPNP and Ir(dpp)₃ is

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An electric current was passed through the device and the properties of the emitted light measured and the results are shown in the table 2 and in figs.18 and 21 to 25 of the drawings as configuration 1.

Example 3

A device was constructed as in example 1 which had the structure as shown in fig. 17b in which (1) is ITO, (2) is CuPc, (3) is α -NPB, (4) is the electroluminescent mixture, (5) is Eu(DBM)₃OPNP, (6) is BCP, (7) is Alq₃ (8) is aluminium. The structure was:-

ITO/CuPc(8nm)/ α -NPB(40nm)/ Ir(diacac)₂(dpp)₂(6%)+CBP+R1(40%)(20nm)
/R1(20nm)/BCP(6nm)/Alq3(20nm)/Al

where Ir(diacac)₃ is iridium di-acetylacetonate and CBP is shown in fig. 4b with R being H and is a host compound.

An electric current was passed through the device and the properties of the emitted light measured and the results are shown in Table 2 and in figs. 19 and 21 to 25 of the drawings as configuration 2.

Example 4

A device was constructed as in example 1 which had the structure of fig. 17a and consisted of

- 5 ITO/CuPc(8nm)/ α -NPB(40nm)/R1(40%)+Ir(acac)₃(6%)+CBP(20nm)/BCP(6nm)/Alq3(20nm)/Al

where Ir(acac)₃ is iridium acetylacetonate and BCP is bathocupron.

- 10 An electric current was passed through the device and the properties of the emitted light measured and the results are shown in Table 2 and in figs. 20 to 25 of the drawings as configuration 3.

Table 2

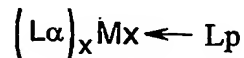
Best Current Efficiency			
Ref.	cd A ⁻¹	x	y
Example 1	3.0	0.63	0.35
Example 2	1.8	0.66	0.33
Example 3	0.8	0.63	0.34

Claims

1. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of a first electroluminescent metal complex or organo metallic complex, (iii) a layer of a second metal complex or organo metallic complex and (iv) a second electrode and in which the band gap of the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the first electroluminescent metal complex or organo metallic complex.
2. An electroluminescent device as claimed in claim 1 in which the metal in the first and second electroluminescent metal complex or organo metallic complex is selected from Sm(III), Eu(II), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), U(III), U(VI)O₂, Tm(III), Th(IV), Ce (III), Ce(IV), Pr(III), Nd(III), Pm(III), Dy(III), Ho(III), Er(III).
3. An electroluminescent device as claimed in claim 1 in which the metal in the first electroluminescent metal complex or organo metallic complex is europium or terbium and the metal in the second electroluminescent metal complex or organo metallic complex is gadolinium or cerium.
4. An electroluminescent device as claimed in claim 1 or 2 in which the metal in the first electroluminescent metal complex or organo metallic complex and the metal in the second electroluminescent metal complex or organo metallic complex are the same.
5. An electroluminescent device as claimed in any one of claims 1 to 4 in which there are more than one layer of each of the first and second electroluminescent metal complex or organo metallic complexes arranged alternatively.
6. An electroluminescent device as claimed in any one of claims 1 to 5 in which the first electroluminescent metal complex or organo metallic complex has the formula $(La)_nM1$ where La is an organic complex M1 is the metal and n is the valence state of M1 and the second electroluminescent metal complex or organo metallic complex has

the formula $(L\alpha)_nM2$ where $L\alpha$ is an organic complex, $M2$ is the metal and n is the valence state of $M2$.

7. An electroluminescent device as claimed in any one of claims 1 to 5 in which the metal complex or organo metallic complexes have the formula



(A)

where Mx , x , $L\alpha$ and Lp are as defined herein and the ligands $L\alpha$ can be the same or different and there can be a plurality of ligands Lp which can be the same or different.

10

8. An electroluminescent device as claimed in any one of claims 1 to 4 in which at least one of the metal complex or organo metallic complexes have the formula $(L\alpha)_n MxM3$ where $M3$ is a non rare earth metal, $L\alpha$ is as defined herein and n is the combined valence state of Mx and $M3$.

15

9. An electroluminescent device as claimed in any one of claims 1 to 4 in which at least one of the metal complex or organo metallic complexes have the formula $(L\alpha)_n MxM3(Lp)$.

20

10. An electroluminescent device as claimed in claim 9 in which the metal $M3$ is any metal which is not a rare earth, transition metal, lanthanide or an actinide.

25

11. An electroluminescent device as claimed in claim 9 in which the metal $M3$ is selected from lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states, e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV),

- 28 -

cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.

12. An electroluminescent device as claimed in any one of claims 1 to 11 in which $L\alpha$ is of formula (I) to (XVII) herein.

13. An electroluminescent device as claimed in any one of claims 1 to 11 in which Lp is of formula (XVIII) to (XXV) herein or figs. 1 to 9 of the drawings

14. An electroluminescent device as claimed in any one of claims 1 to 13 in which $L\alpha$ is selected from tripyridyl and TMHD, and TMHD complexes, α , α' , α'' tripyridyl and Lp is selected from crown ethers, cyclans, cryptans phthalocyanans, porphyrins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA.

15. An electroluminescent device as claimed in any one of claims 1 to 14 in which the europium complex is $\text{Eu}(\text{DBM})_3\text{OPNP}$.

16. An electroluminescent device as claimed in any one of claims 1 to 15 in which the gadolinium complex is $\text{Gd}(\text{DBM})_3\text{Phen}$.

17. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex and (iii) a second electrode.

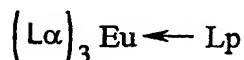
18. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo metallic complex, (iii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex and (iv) a second electrode.

19. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex, (iii) a layer of an electroluminescent europium metal complex or organo metallic complex and (iv) a second electrode.

20. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of an electroluminescent europium metal complex or organo metallic complex, (iii) a layer of an electroluminescent europium metal complex or organo metallic complex mixed with an iridium metal complex or organo metallic complex, (iv) a layer of an electroluminescent europium metal complex or organo metallic complex and (v) a second electrode.

21. An electroluminescent device as claimed in any one of claims 17 to 20 in which the europium metal complex or organo metallic complex has the formula $(L\alpha)_3Eu$ where $L\alpha$ is an organic complex.

22. An electroluminescent device as claimed in any one of claims 17 to 19 in which the europium metal complex or organo metallic complex has the formula



(AI)

where $L\alpha$ and Lp are organic ligands and Lp is a neutral ligand, the ligands $L\alpha$ can be the same or different and there can be a plurality of ligands Lp which can be the same or different.

23. An electroluminescent device as claimed in any one of claims 17 to 19 in which the europium metal complex or organo metallic complex has the formula $(L\alpha)_nEuM_2$ where M_2 is a non rare earth metal, $L\alpha$ is as herein and n is the combined valence state of Eu and M_2 .

24. An electroluminescent device as claimed in any one of claims 17 to 19 in which the europium metal complex or organo metallic complex has the formula $(L\alpha)_n Eu M_2 (Lp)$, where Lp is as herein.
- 5 25. An electroluminescent device as claimed in claim 24 in which the metal M_2 is any metal which is not a rare earth, transition metal, lanthanide or an actinide.
26. An electroluminescent device as claimed in claim 24 in which the metal M_2 is selected from lithium, sodium, potassium, rubidium, caesium, beryllium, magnesium, calcium, strontium, barium, boron, copper (I), copper (II), silver, gold, zinc, cadmium, boron, aluminium, gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states, e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, hafnium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium.
- 10 15
27. An electroluminescent device as claimed in any one of claims 17 to 26 in which $L\alpha$ is of formula (I) to (XVII) herein.
- 20
28. An electroluminescent device as claimed in any one of claims 17 to 26 in which Lp is of formula (XVIII) to (XXV) herein or figs. 1 to 9 of the drawings.
29. An electroluminescent device as claimed in any one of claims 17 to 28 in which $L\alpha$ is selected from tripyridyl and TMHD, and TMHD complexes, α , α' , α'' tripyridyl and Lp is selected from crown ethers, cyclans, cryptans phthalocyanans, porphyrins ethylene diamine tetramine (EDTA), DCTA, DTPA and TTHA.
- 25
30. An electroluminescent device as claimed in any one of claims 17 to 29 in which the europium complex is $Eu(DBM)_3OPNP$.
- 30

31. An electroluminescent device as claimed any one of claims 1 to 30 in which there is a layer of a hole transmitting material between the first electrode and the electroluminescent layer.

5

32. An electroluminescent device as claimed in any one of claims 1 to 30 in which the hole transmitting material is an aromatic amine complex.

10 33. An electroluminescent device as claimed in any one of claims 1 to 30 in which the hole transmitting material is a polyaromatic amine complex.

15 34. An electroluminescent device as claimed in any one of claims 1 to 30 in which the hole transmitting material is a film of a polymer selected from poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes and substituted polysilanes.

20 35. An electroluminescent device as claimed in any one of claims 1 to 30 in which the hole transmitting material is a film of a compound of formula (XXVI) or (XXVII) herein or as in figures 4 to 8 of the drawings.

25 36. An electroluminescent device as claimed in any one of claims 1 to 30 in which the hole transmitting material is a copolymer of aniline, a copolymer of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with an amino anthracene.

37. An electroluminescent device as claimed in any one of claims 1 to 30 in which the hole transmitting material is a conjugated polymer.

38. An electroluminescent device as claimed in claim 37 in which the conjugated polymer is selected from poly (p-phenylenevinylene)-PPV and copolymers including PPV, poly(2,5 dialkoxyphenylene vinylene), poly (2-methoxy-5-(2-methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.
39. An electroluminescent device as claimed in any one of claims 31 to 38 in which the electroluminescent compound is mixed with the hole transmitting material.
40. An electroluminescent device as claimed in any one of claims 1 to 39 in which there is a layer of an electron transmitting material between the cathode and the electroluminescent compound layer.
41. An electroluminescent device as claimed in claim 40 in which the electron transmitting material is a metal quinolate.
42. An electroluminescent device as claimed in claim 41 in which the metal quinolate is an aluminium quinolate or lithium quinolate.
43. An electroluminescent device as claimed in claim 39 in which the electron transmitting material is of formula $Mx(DBM)_n$ where Mx is a metal and DBM is dibenzoyl methane and n is the valency of Mx.
44. An electroluminescent device as claimed in claim 40 in which the electron transmitting material is a cyano anthracene such as 9,10 dicyano anthracene, a

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polystyrene sulphonate or a compound of formulae shown in figure 2 or 3 of the drawings.

45. An electroluminescent device as claimed in any one of claims 40 to 44 in which
5 the electron transmitting material is mixed with the electroluminescent compound.

46. An electroluminescent device as claimed in any one of the claims 1 to 45 in which the first electrode is a transparent electricity conducting glass electrode.

10 47. An electroluminescent device as claimed in any one of the claims 1 to 46 in which the second electrode is selected from aluminium, calcium, lithium, magnesium and alloys thereof and silver/magnesium alloys.

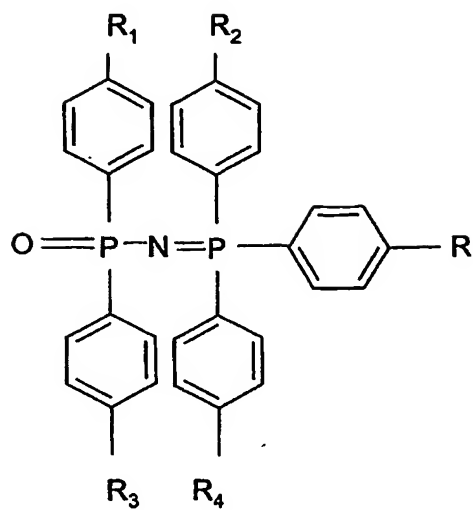


Fig. 1

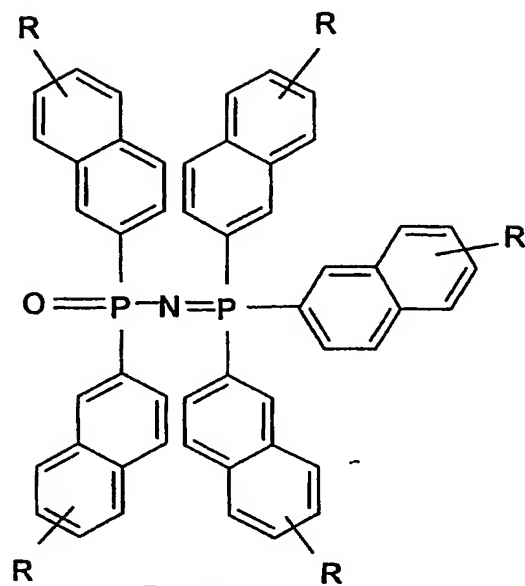


Fig. 2a

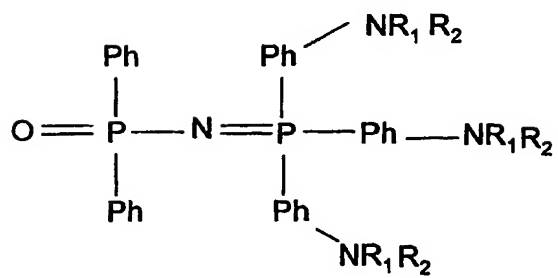


Fig. 2b

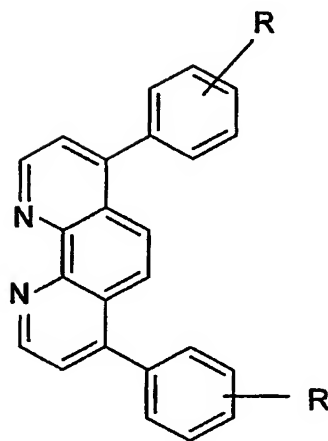


Fig. 3

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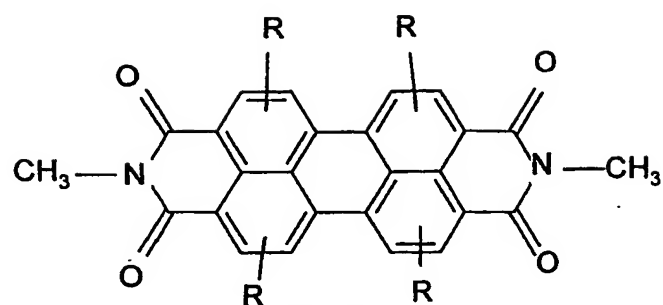


Fig. 4a

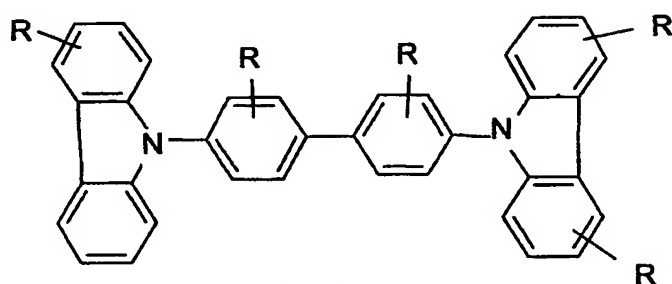


Fig. 4b

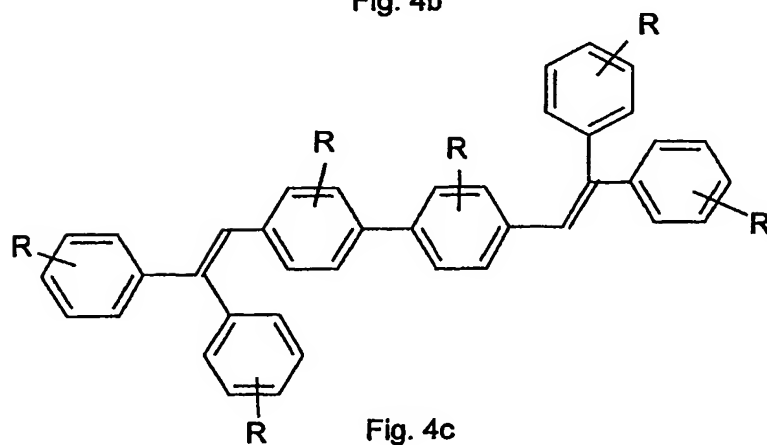


Fig. 4c

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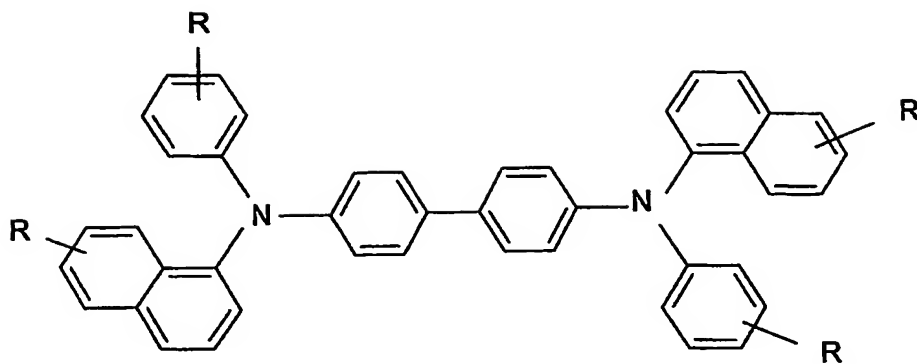


Fig. 4d

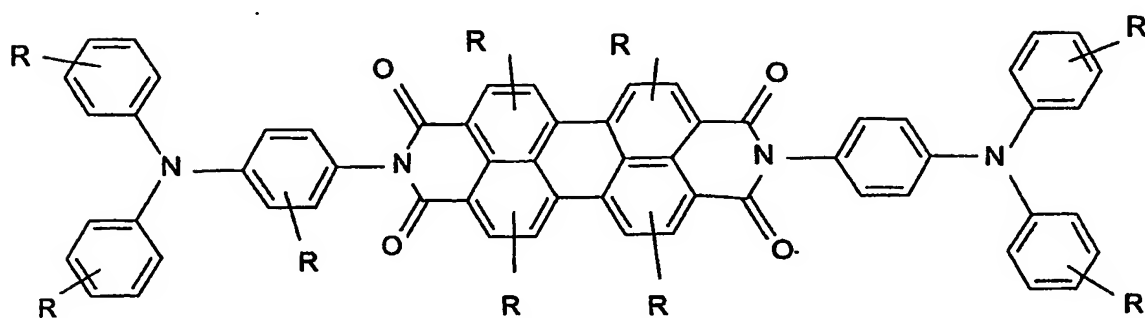


Fig. 4e

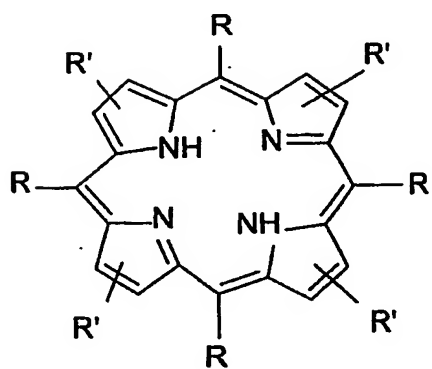


Fig. 4f

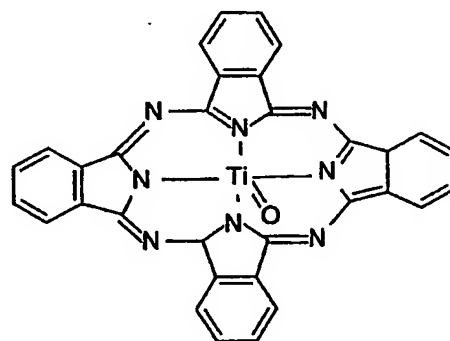


Fig. 4g

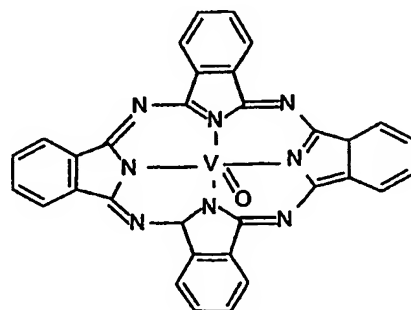


Fig. 4h

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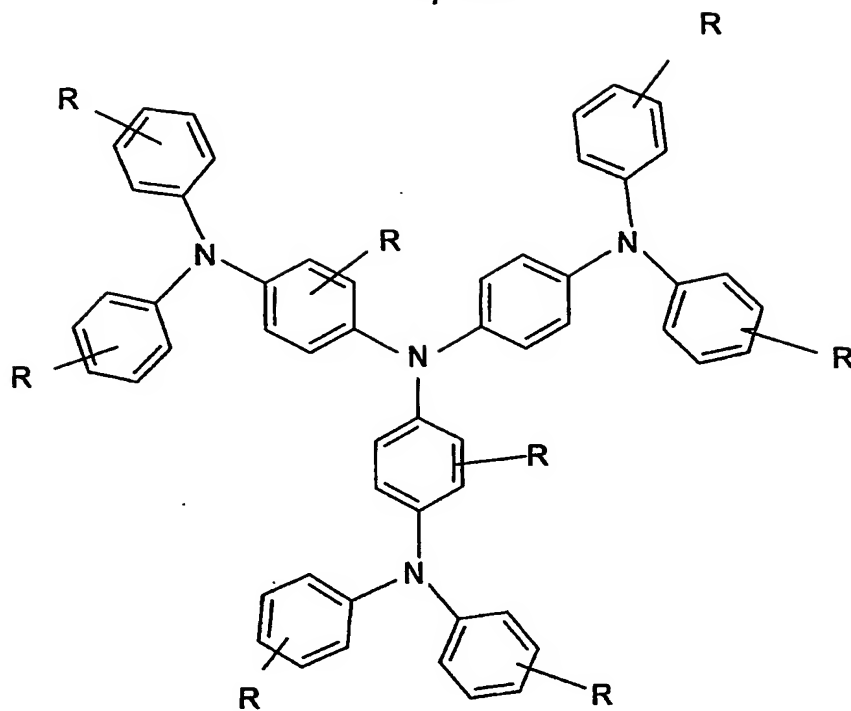


Fig. 4i

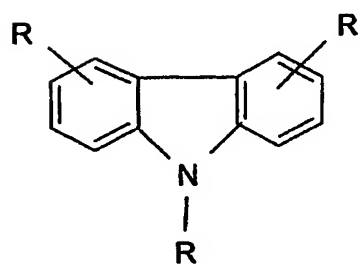


Fig. 4j

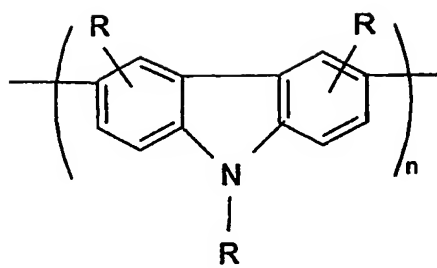


Fig. 4k

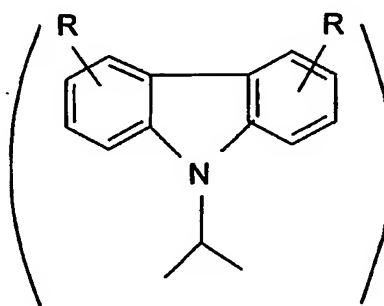


Fig. 4l

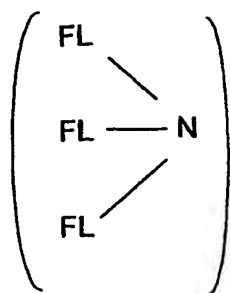


Fig. 5a

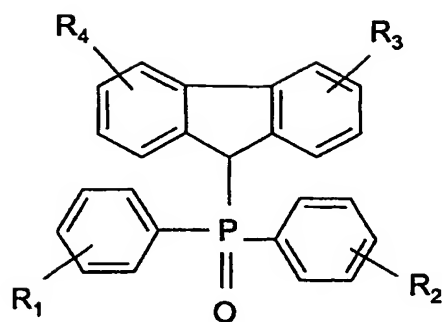


Fig.5b

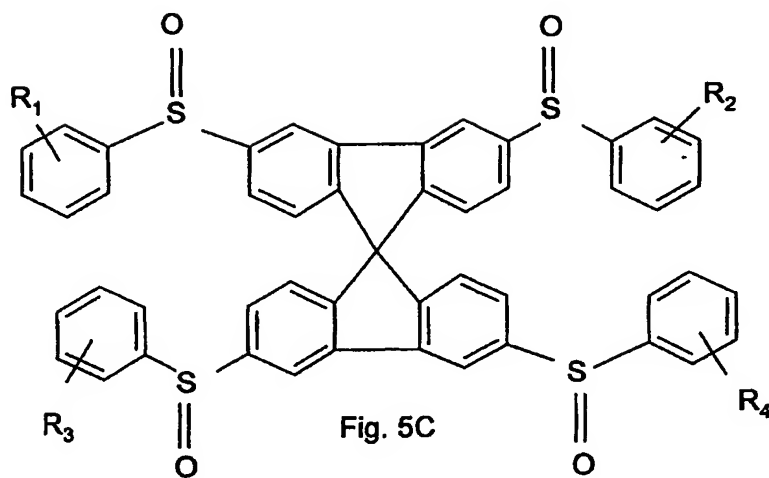


Fig. 5C

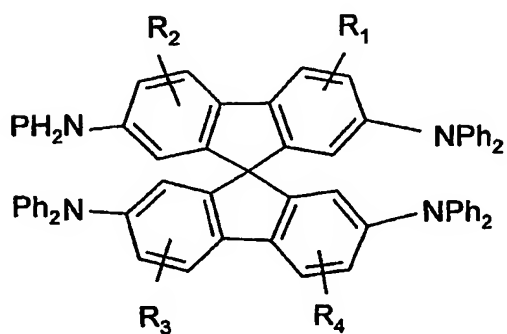


Fig. 5d

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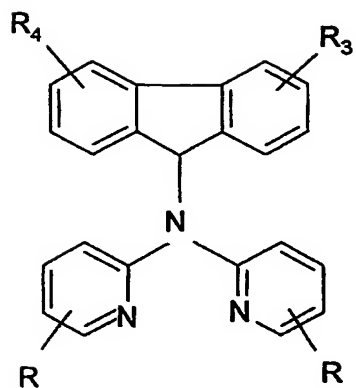


Fig. 5f

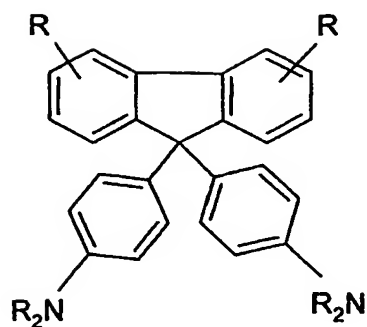


Fig. 5g

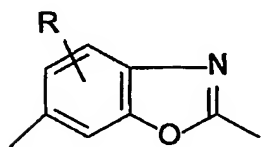


Fig. 6a

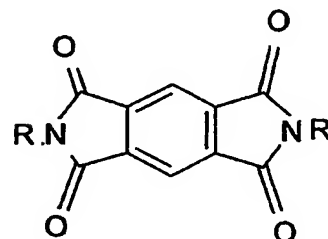


Fig 6b

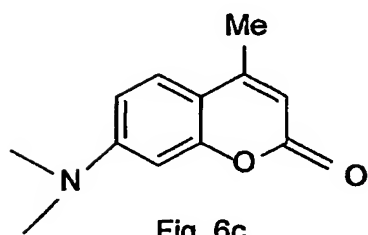


Fig. 6c

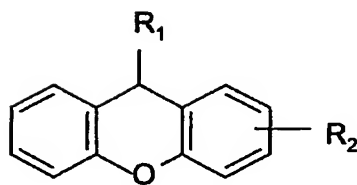


Fig. 6d

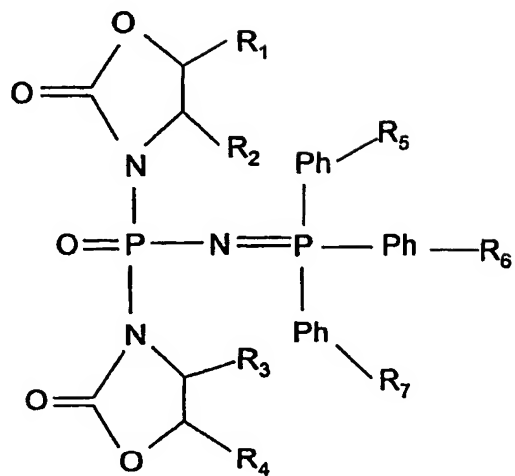


Fig. 6e

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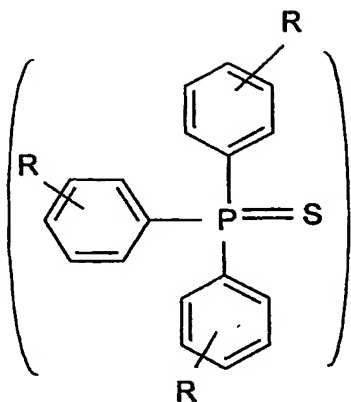


Fig. 7a

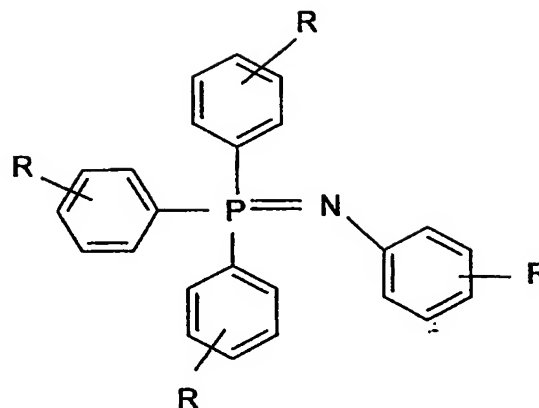


Fig. 7b

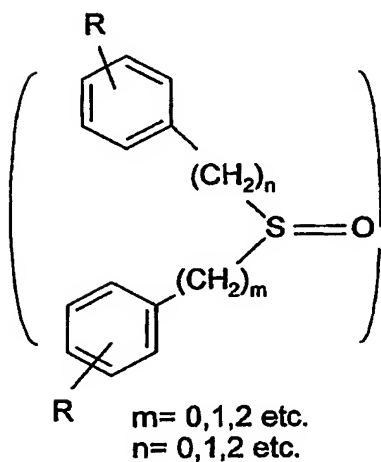


Fig. 7c

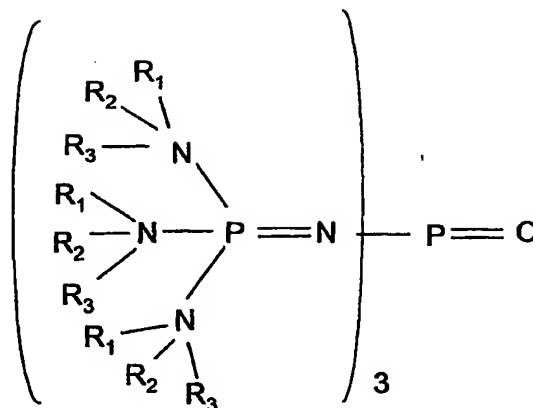


Fig. 7d

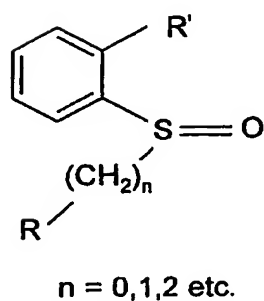


Fig. 7e

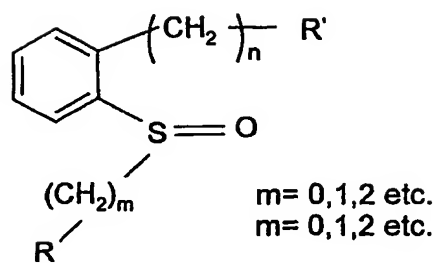


Fig. 7f

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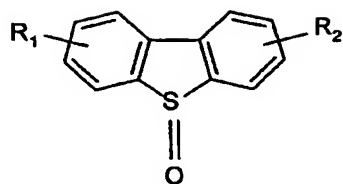


Fig. 8a

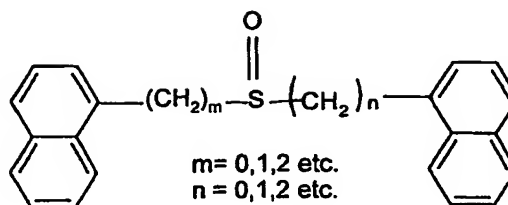


Fig. 8b

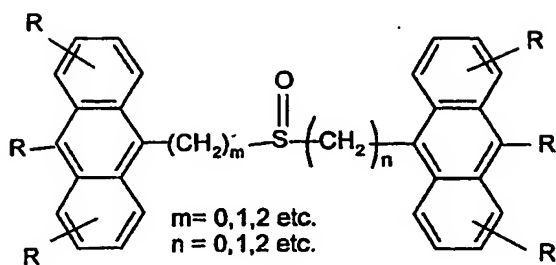


Fig. 8c

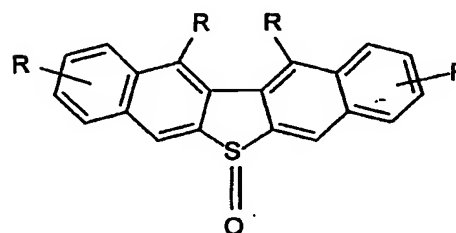


Fig. 8d

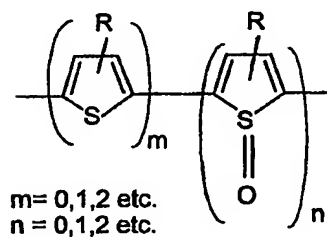


Fig. 8e

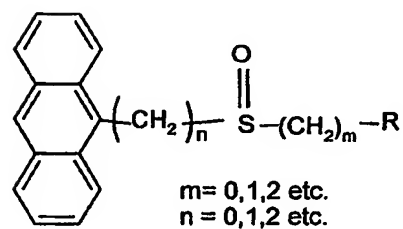


Fig. 8f

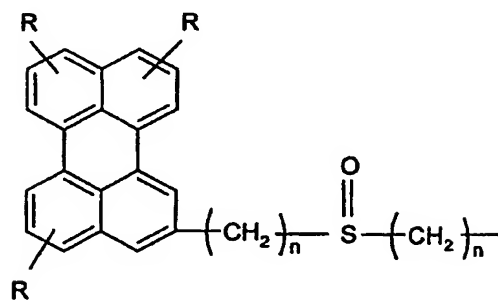


Fig. 8g

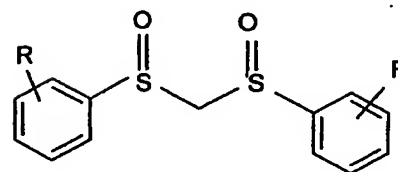
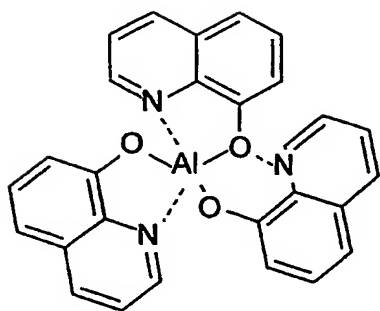
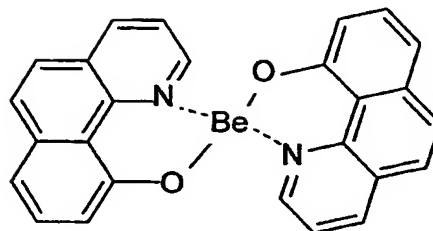


Fig. 8h

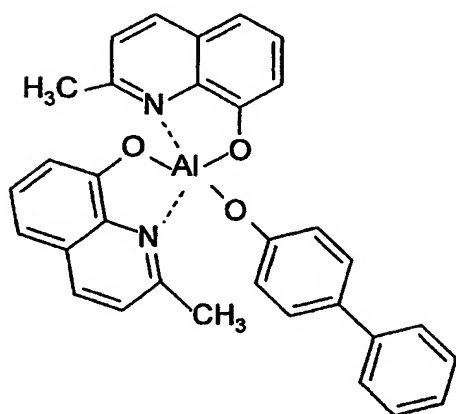
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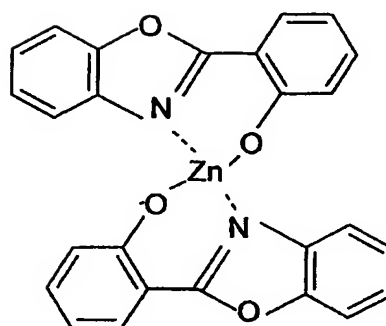
Alq



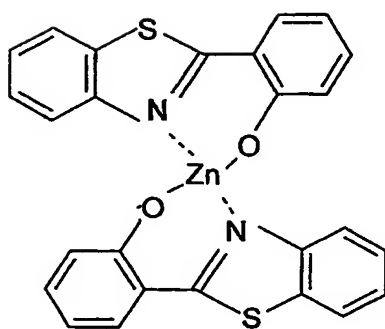
Bebq



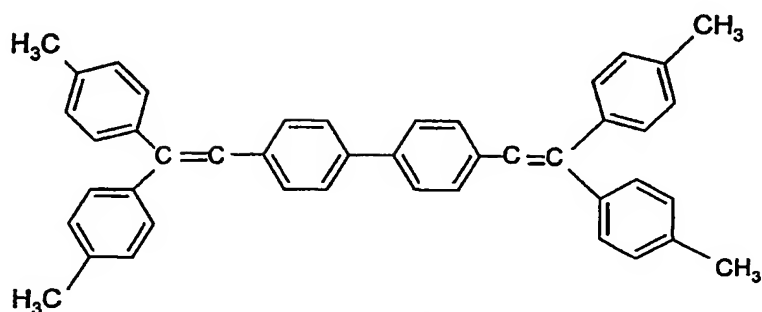
BAlq1



ZnPBO



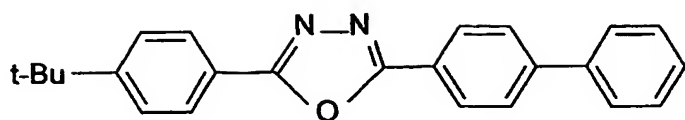
ZnPBT



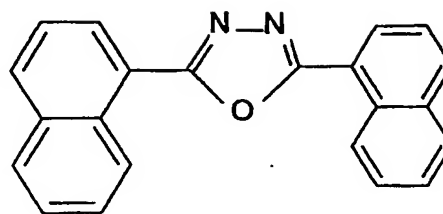
DTVb1

Fig. 9

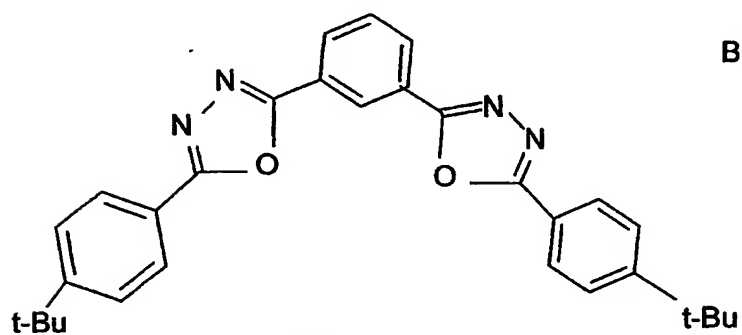
10/25



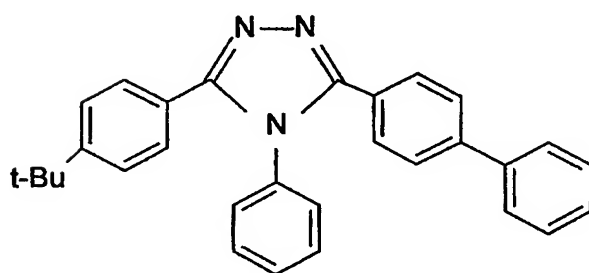
t-Bu-PBD



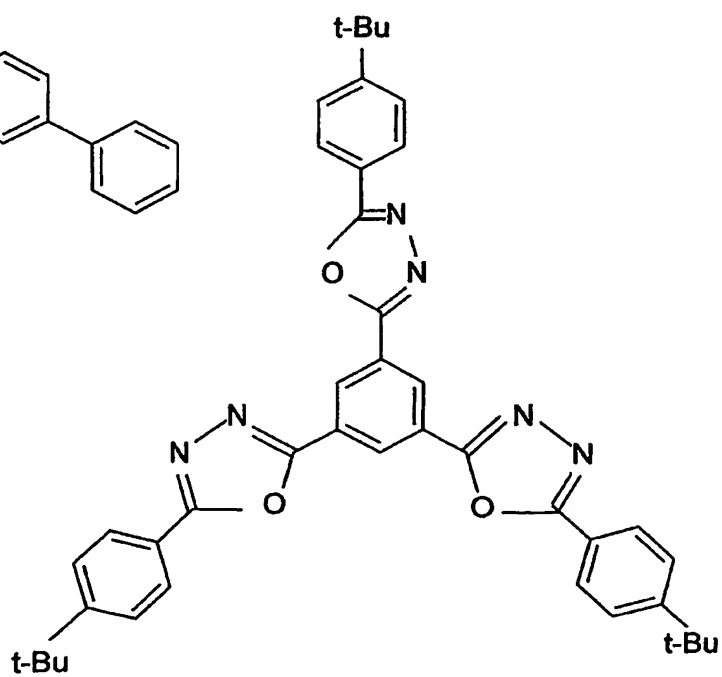
BND



OXD-7



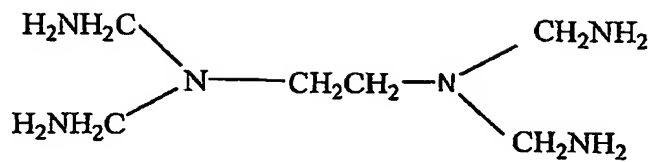
TAZ



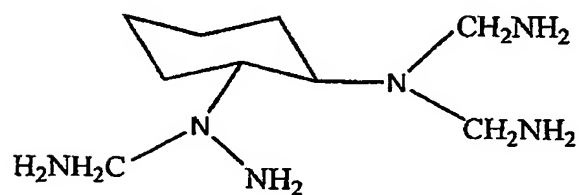
OXD- Star

Fig. 10

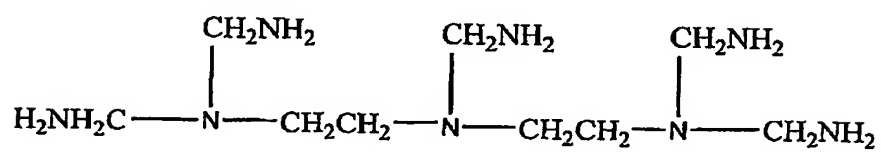
11/25



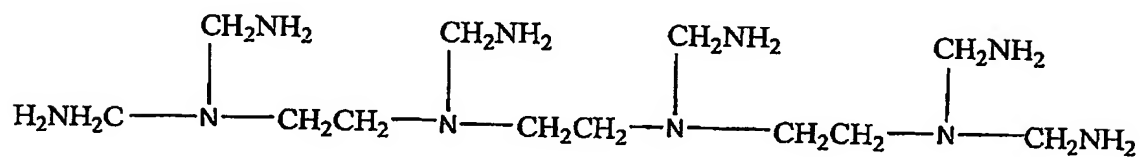
EDTA



DCTA



DTPA



TTHA

Fig. 11

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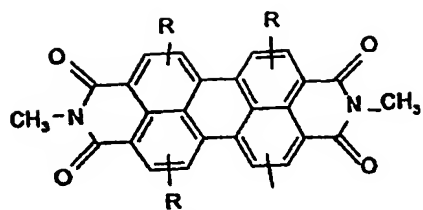


Fig. 12a

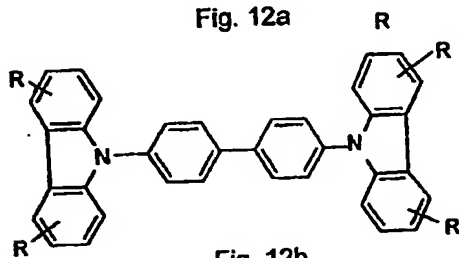


Fig. 12b

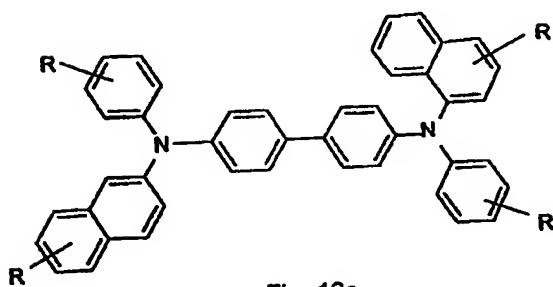


Fig. 12c

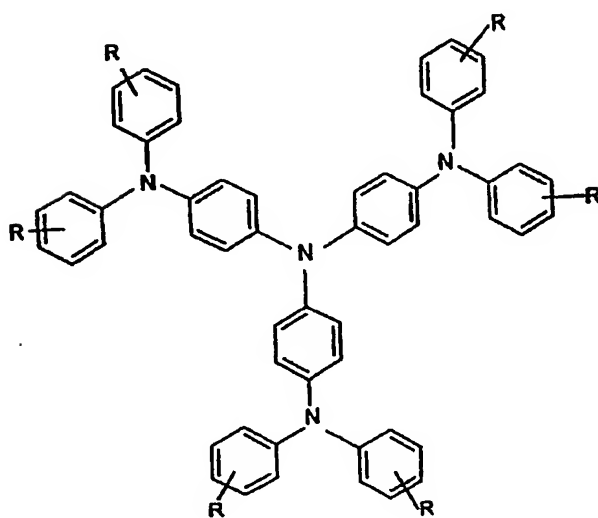


Fig. 12d

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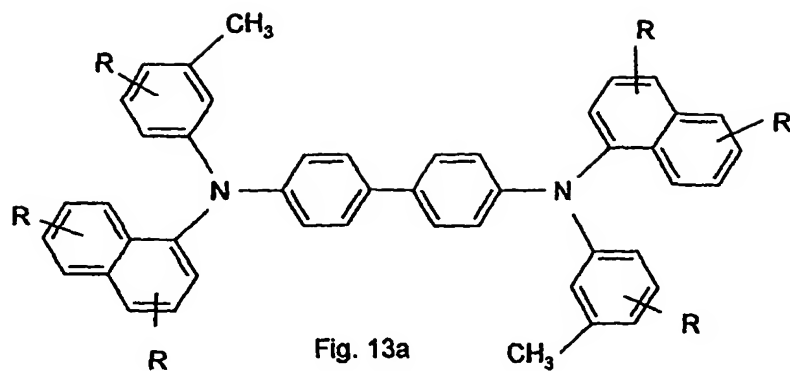


Fig. 13a

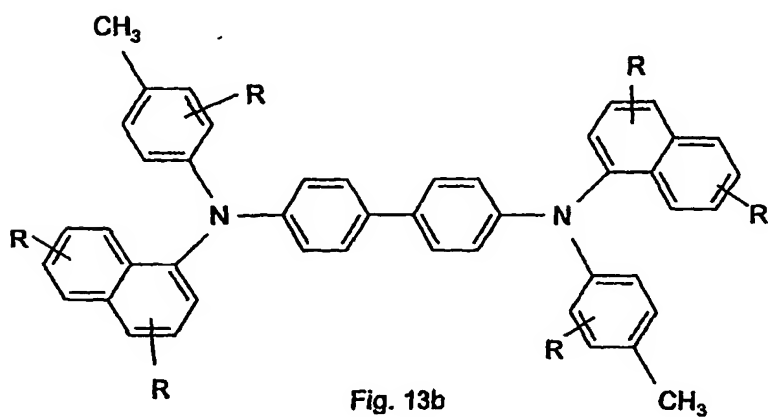


Fig. 13b

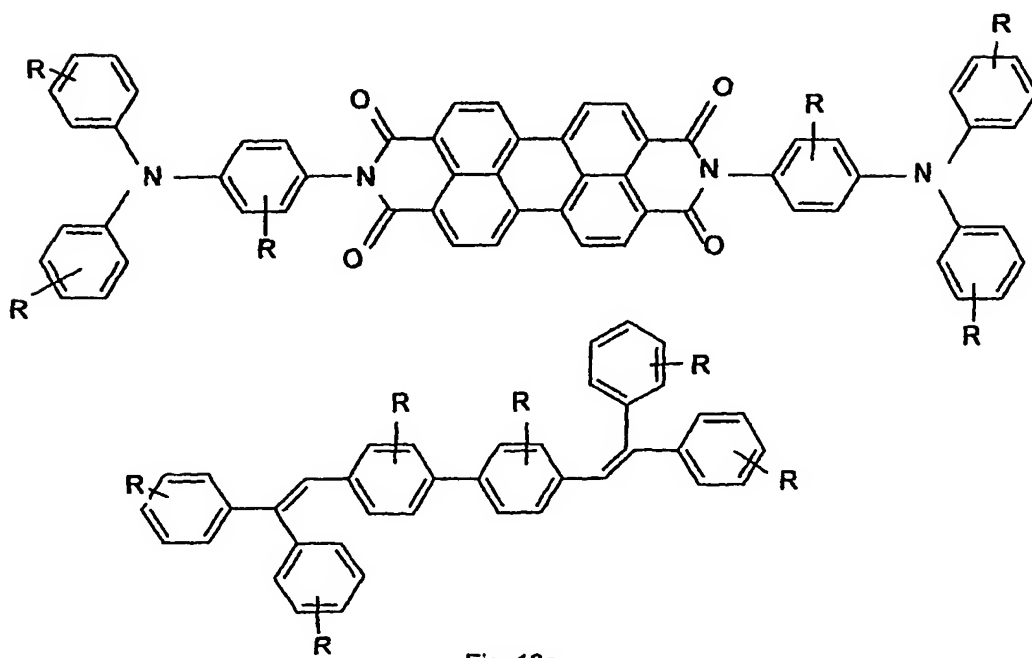


Fig. 13c

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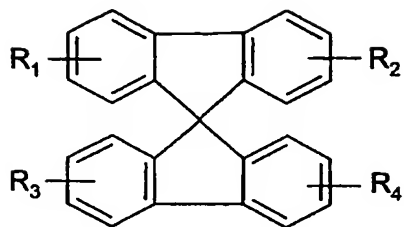


Fig. 14a

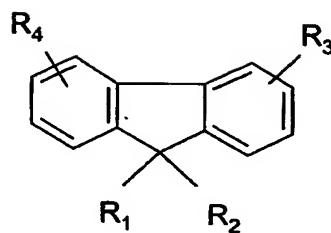
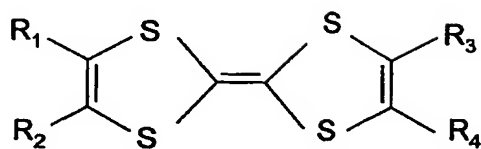


Fig. 14b



or

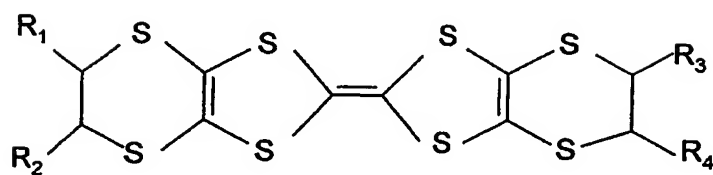


Fig. 14c

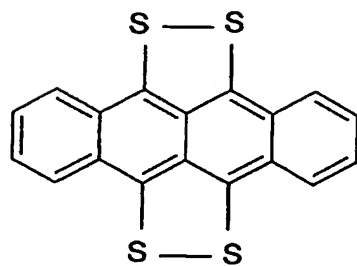


Fig. 14d

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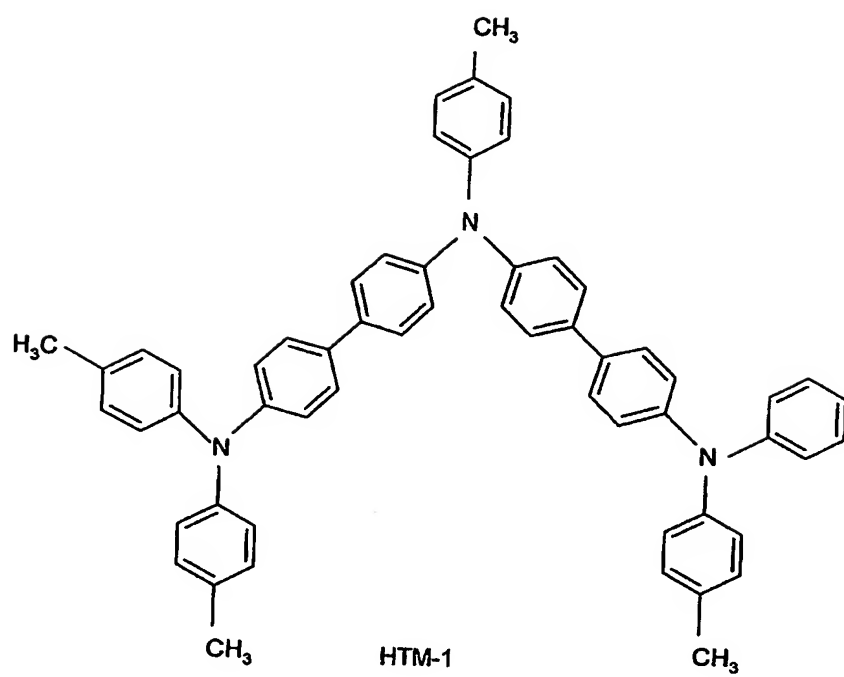


Fig. 15a

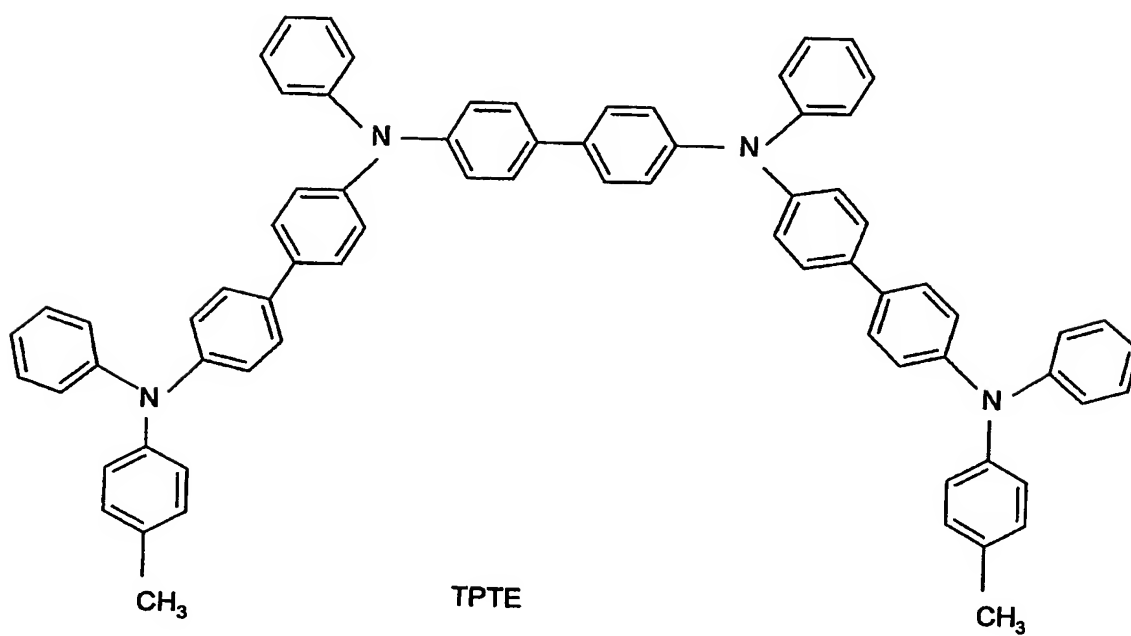


Fig. 15b

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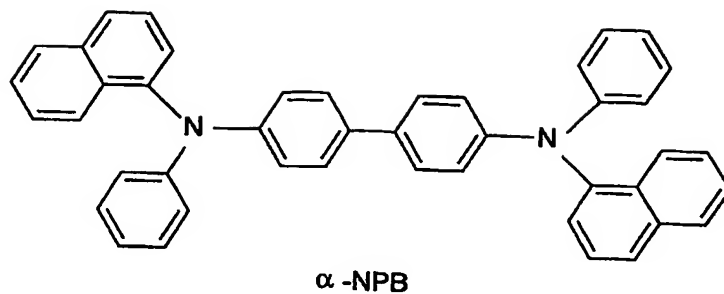
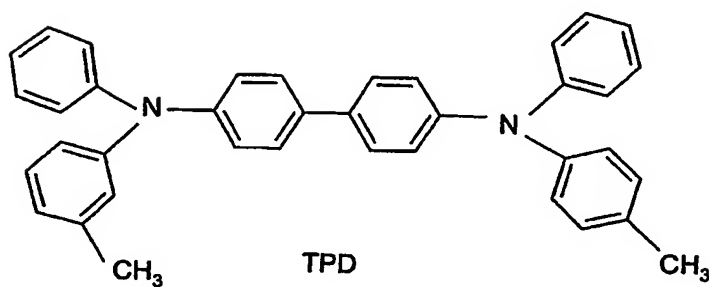
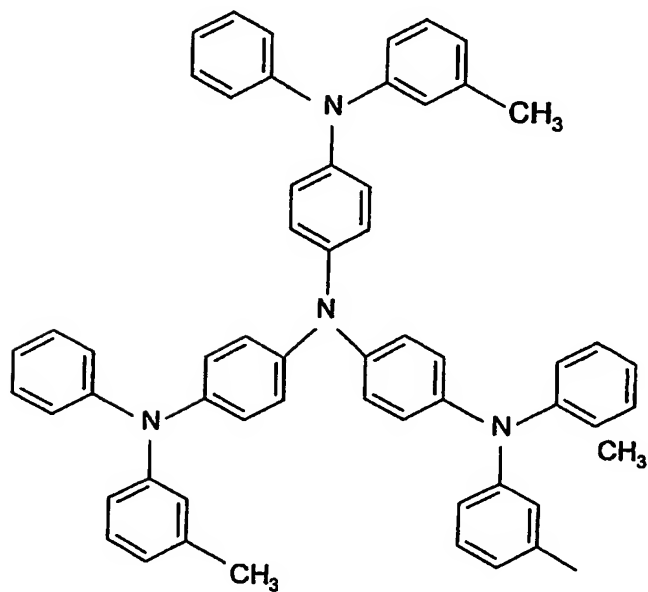
 α -NPB

Fig. 16a



TPD

Fig. 16b



mTADATA

Fig. 16c

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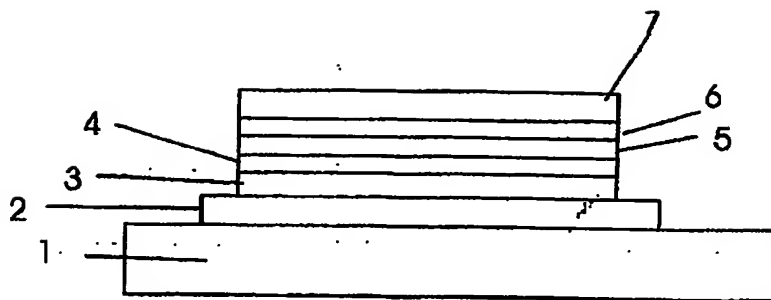


Fig. 17a

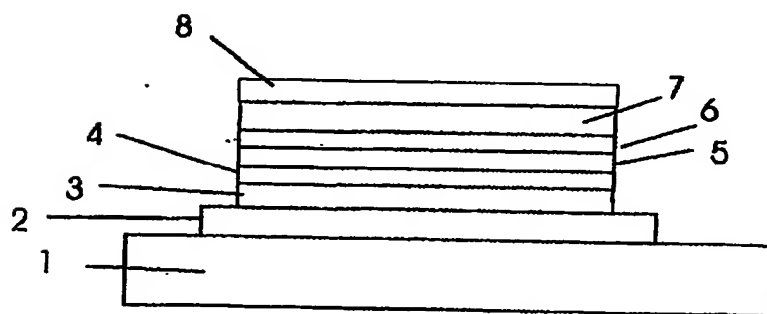
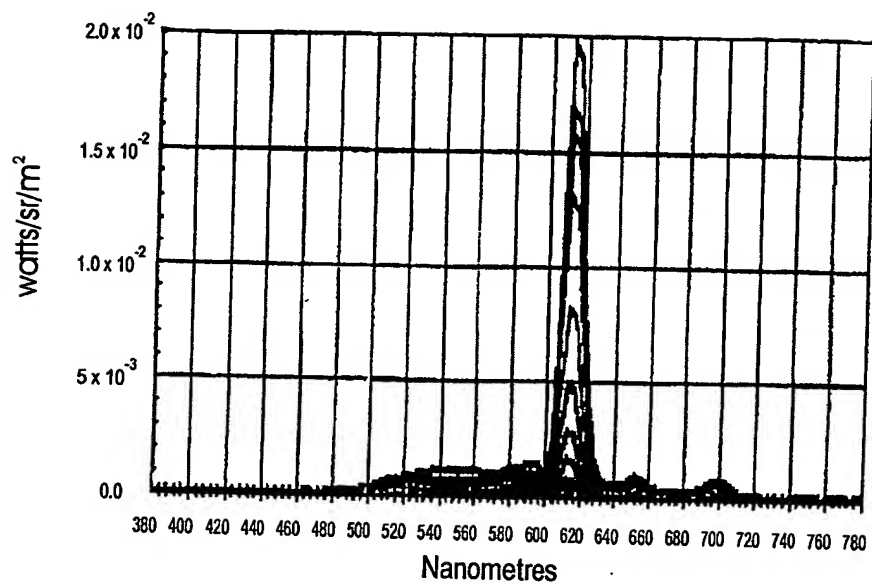


Fig. 17b

Device of example 2



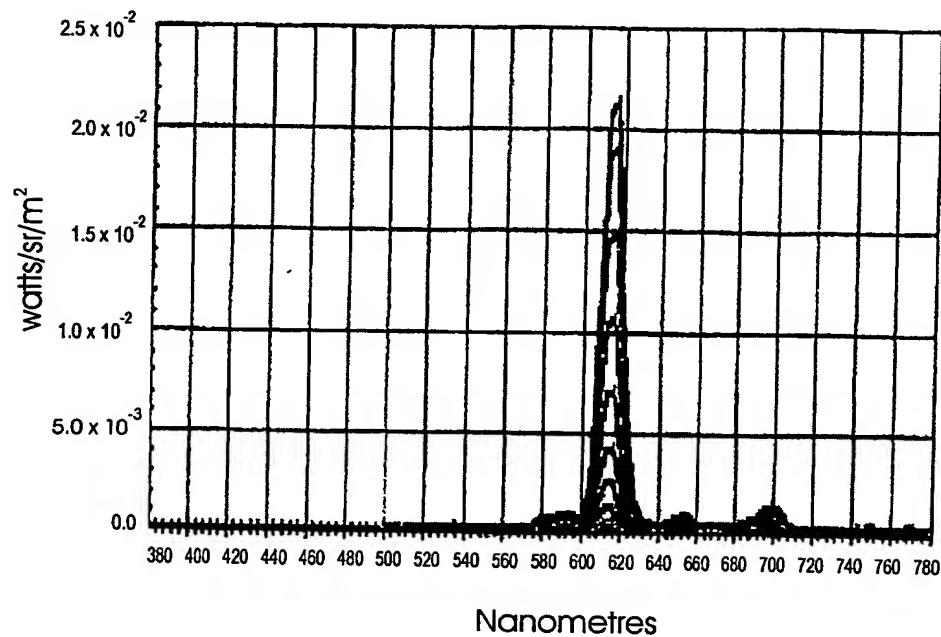
Voltage / V	Colour Co-ordinates	
	x	y
22	0.61	0.33
24	0.62	0.33
26	0.62	0.34
28	0.63	0.35
30	0.63	0.35
33	0.63	0.35
36	0.63	0.35
39	0.63	0.35
42	0.63	0.35
46	0.62	0.36
50	0.62	0.36
54	0.61	0.37
58	0.61	0.37
62	0.60	0.38
66	0.59	0.39

Fig. 18

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Device of example

Spectral Radiance

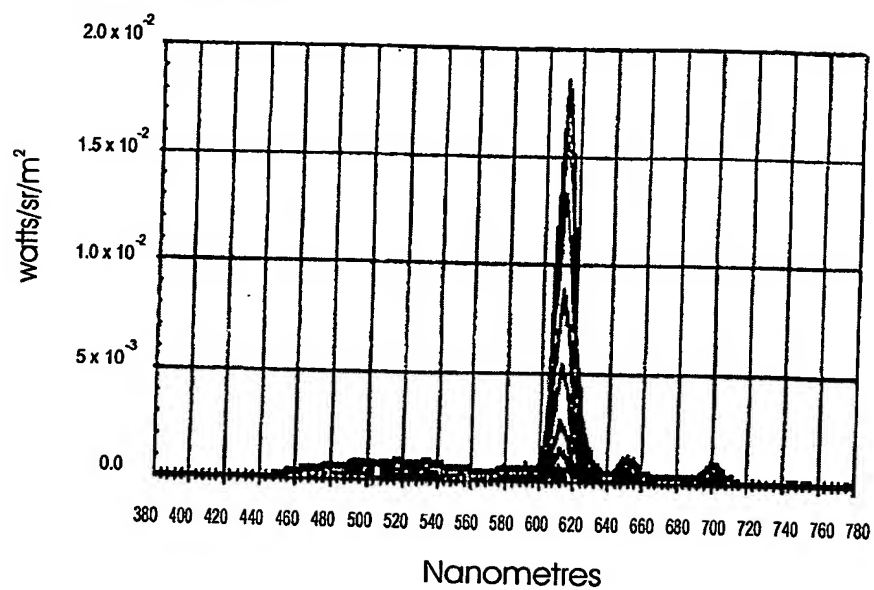


Voltage / V	Colour Co-ordinates	
	x	y
30	0.62	0.32
33	0.62	0.32
36	0.62	0.33
39	0.66	0.33
42	0.66	0.33
46	0.66	0.33
50	0.66	0.33
54	0.66	0.33
58	0.66	0.33
62	0.66	0.33
67	0.66	0.33
72	0.65	0.33
77	0.65	0.33
82	0.65	0.33

Fig. 19

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Device of Example 4



Voltage / V	Colour Co-ordinates	
	x	y
30	0.57	0.34
33	0.60	0.32
36	0.62	0.33
39	0.2	0.33
42	0.63	0.34
45	0.63	0.34
48	0.63	0.34
51	0.63	0.34
55	0.63	0.34
59	0.63	0.34
63	0.62	0.34
67	0.59	0.35
71	0.57	0.36

Fig. 20

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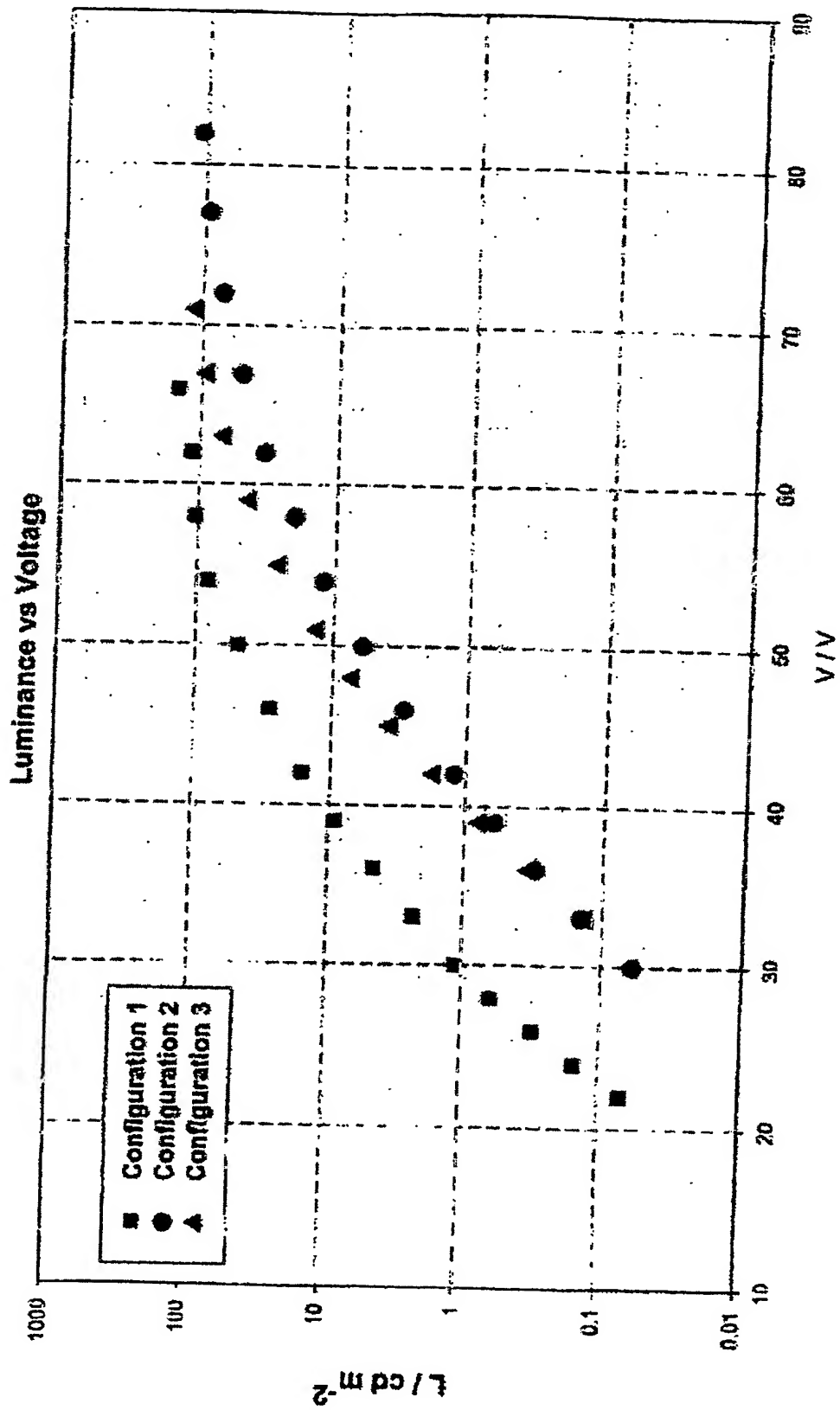


Fig. 21

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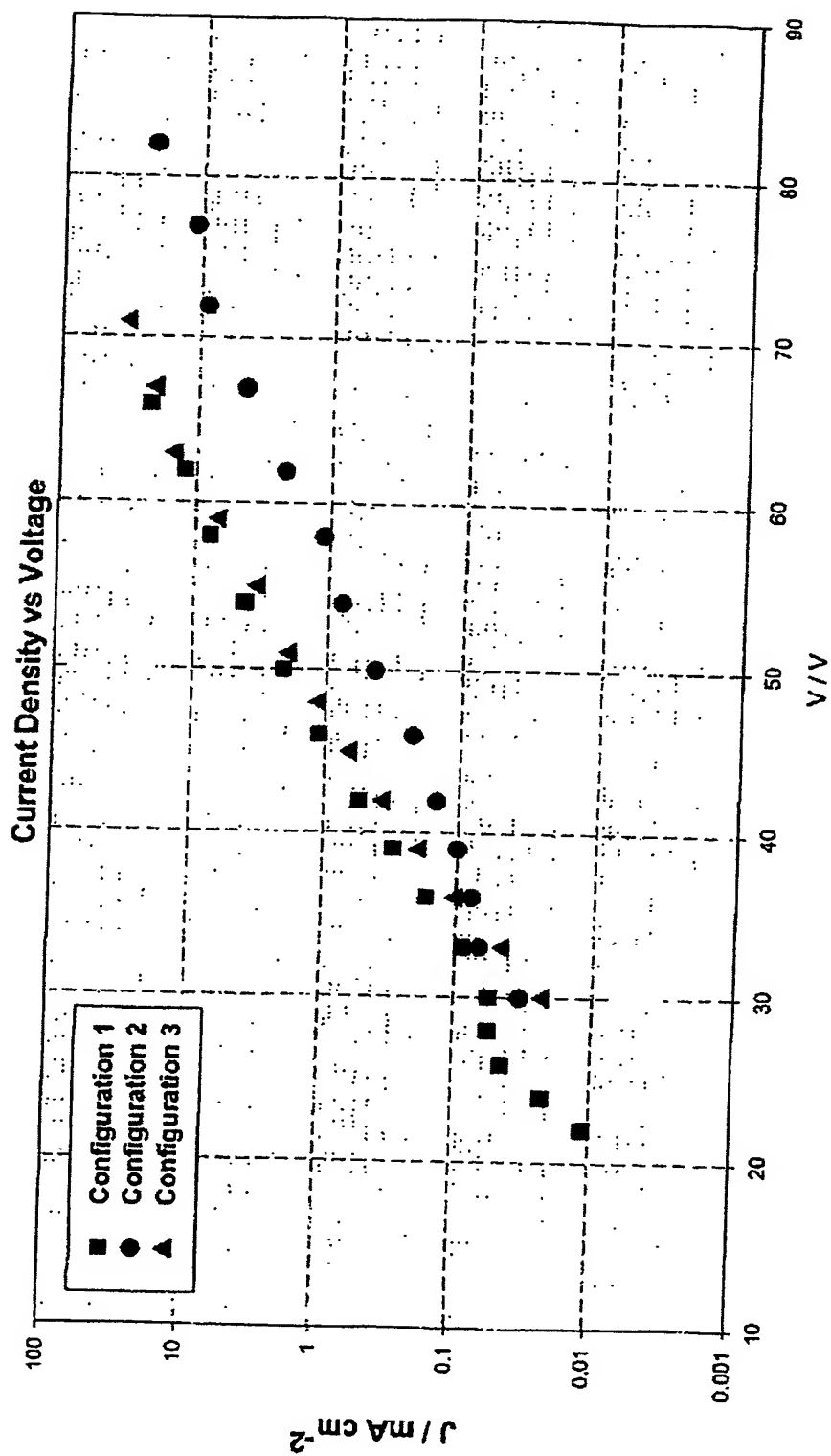


Fig. 22

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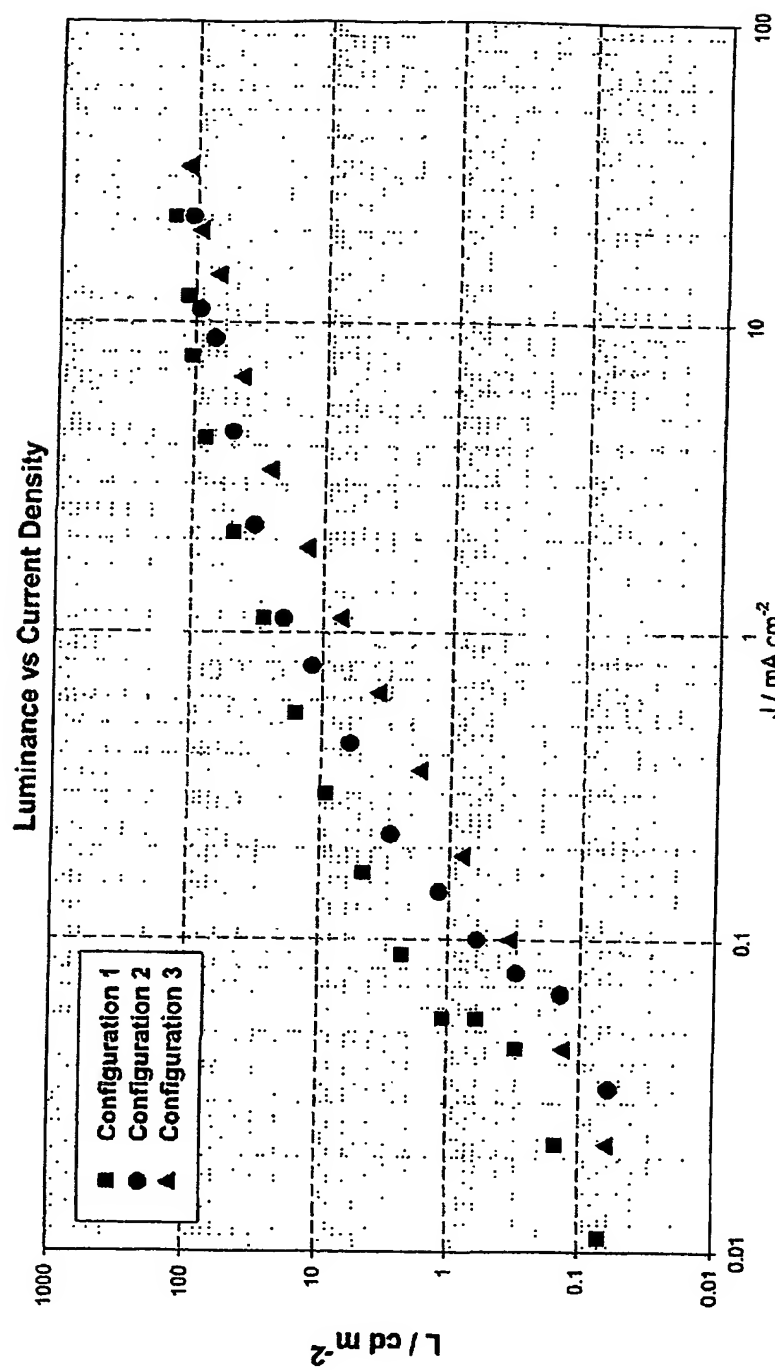


Fig. 23

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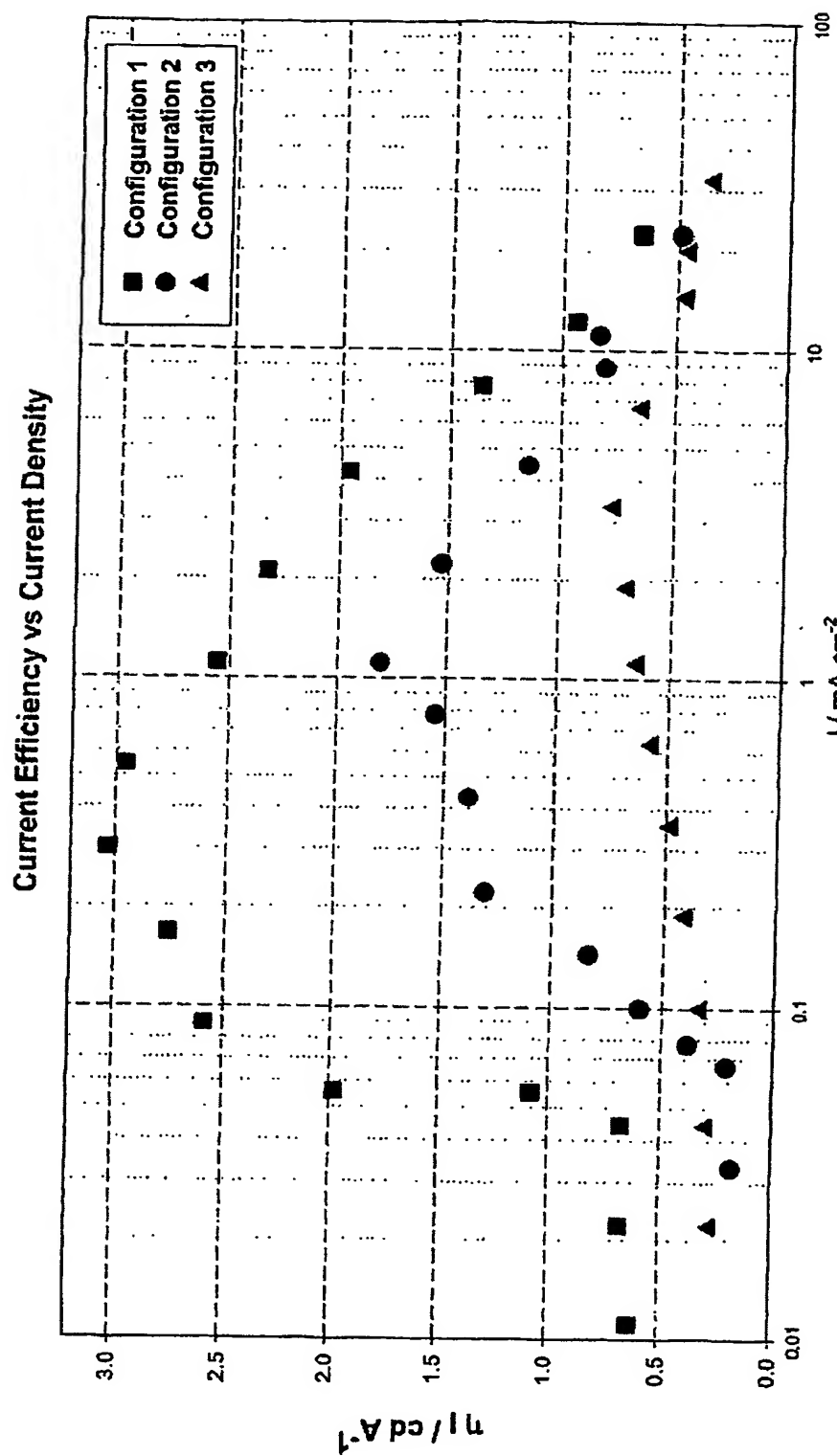


Fig. 24

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J vs V Characteristics

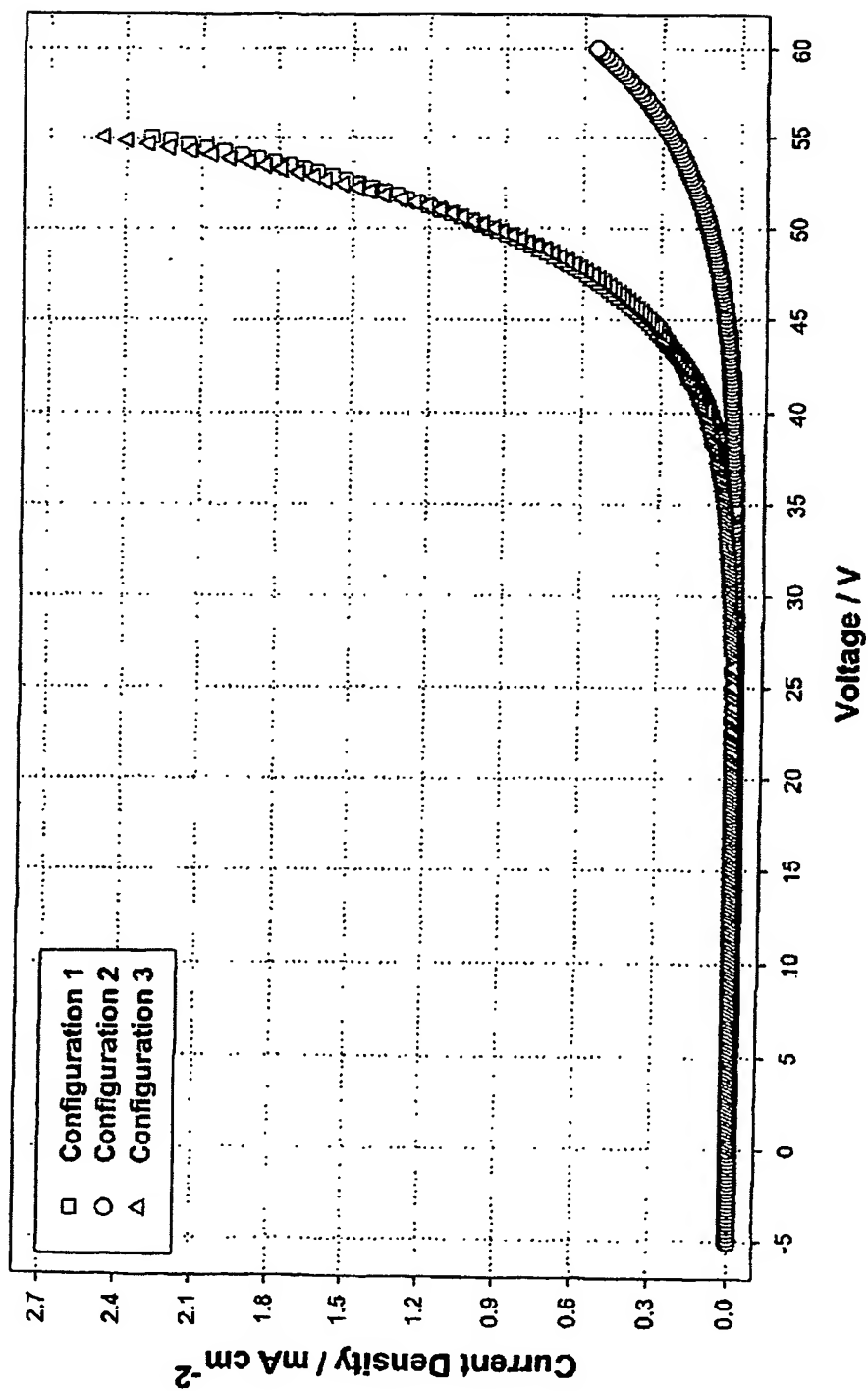


Fig. 25



24 JUN 2005

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H05B 33/14, H01L 51/20(21) International Application Number:
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0230077.0 24 December 2002 (24.12.2002) GB(71) Applicant (for all designated States except US): **ELAM-T LIMITED** [GB/GB]; 103 Borough Road, London SE1 0AA (GB).

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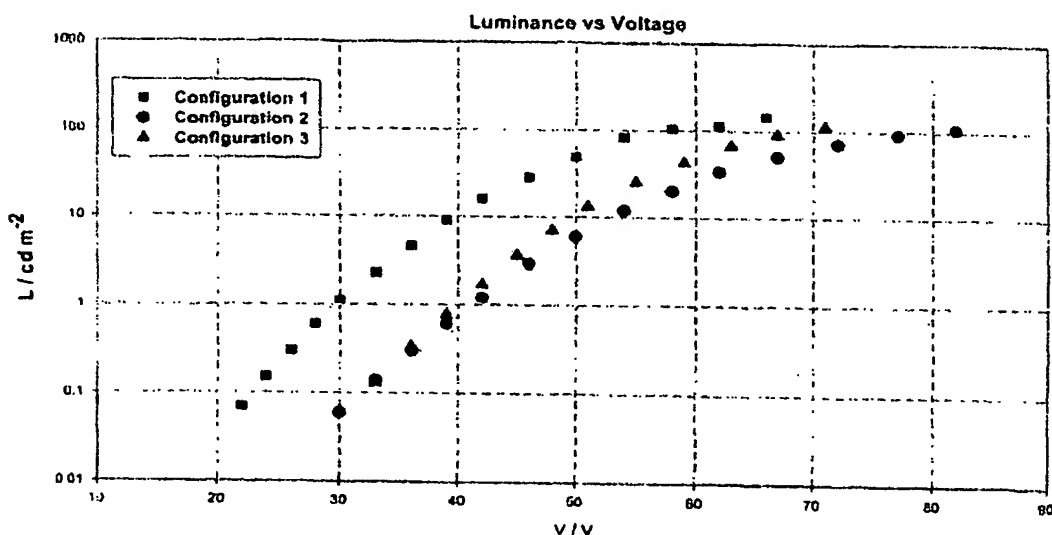
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KANDAPPU, Vijendra [GB/GB]; 81 Roseberry Avenue,Manor Park, London E12 6PY (GB). **GANESHAMURUGAN, Subramaniam** [LK/GB]; 135 Antill Road, London N15 4BB (GB). **PARAMASWARA, Gnanamoly** [LK/GB]; 19 Southway, Totteridge, London N20 8EB (GB).(74) Agent: **COHEN, Alan, Nicol**; 2 Grove Place, Tatsfield, Nr. Westerham, Kent TN16 2BB (GB).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.(84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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[Continued on next page]

(54) Title: ELECTROLUMINESCENT MATERIALS AND DEVICES



(57) Abstract: An improved electroluminescent device has a layer of a first electroluminescent metal complex or organo metallic complex and a layer of a second metal complex or organo metallic complex in which the band gap of the metal in the second electroluminescent metal complex or organo metallic complex is larger than the band gap of the metal in the first electroluminescent metal complex or organo metallic complex.



(88) Date of publication of the international search report:
29 December 2004

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/GB 03/05663

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/06 H05B33/14 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K H05B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/58037 A (KATHIRGAMANATHAN POOPATHY ; SOUTH BANK UNIV ENTPR LTD (GB)) 23 December 1998 (1998-12-23) page 5, paragraph 5 - paragraph 6; claims 1-29; example 6; table 2	1,2, 4-15, 31-47
X	WO 00/26323 A (KATHIRGAMANATHAN POOPATHY ; SOUTH BANK UNIV ENTPR LTD (GB)) 11 May 2000 (2000-05-11) claims 2,3,25	1-14, 31-47
X	WO 02/33022 A (GEN ELECTRIC) 25 April 2002 (2002-04-25) page 6, line 23 - line 25; claims 1,2	1-14, 31-47
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

24 May 2004

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Inte Application No

PCT/GB 03/05663

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/44851 A (KATHIRGAMANATHAN POOPATHY ; SOUTH BANK UNIV ENTPR LTD (GB)) 3 August 2000 (2000-08-03) claim 9 -----	1-14, 31-47
P,X	WO 03/093394 A (KATHIRGAMANATHAN POOPATHY ; ELAM T LTD (GB)) 13 November 2003 (2003-11-13) claims 1,4,10,12 -----	1-14, 31-47
X	WO 02/087288 A (KATHIRGAMANATHAN POOPATHY ; ELAM T LTD (GB)) 31 October 2002 (2002-10-31) claims 1-3,12; example -----	1,2, 4-14, 31-47
X	WO 98/55561 A (CHRISTOU VICTOR ; ISIS INNOVATION (GB)) 10 December 1998 (1998-12-10) page 13, line 25 - page 14, line 2; claims 1,12 -----	1-14, 31-47
A	WO 02/43446 A (KATHIRGAMANATHAN POOPATHY ; ELAM T LIMIED (GB)) 30 May 2002 (2002-05-30) the whole document -----	1-16, 31-47
A	US 4 443 380 A (YAMAZOE KATSUHIKO ET AL) 17 April 1984 (1984-04-17) comparative example 7 -----	1-16, 31-47

INTERNATIONAL SEARCH REPORT

national application No.
PCT/GB 03/05663

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1(part), 2(part), 3-16, 31(part) -47(part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: -

Present claims 1-47 relate to an extremely large number of possible devices. Support within the meaning of Article 6 PCT and or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the devices claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the devices prepared in the examples.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1 (part), 2 (part), 3-16, 31 (part) - 47 (part)

An electroluminescent device comprising a first electroluminescent metal complex in which the metal is europium or terbium and a second electroluminescent metal complex in which the metal is gadolinium or cerium

2. claims: 1 (part), 2 (part), 17-30, 31 (part) - 47 (part)

An electroluminescent device comprising an electroluminescent layer comprising an europium complex mixed with an iridium complex

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/GB 03/05663

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inventor's application No

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